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Disposal of Solid Residue from Fluidized-Bed Combustion Engineering and Laboratory Studies

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DISPOSAL OF SOLID RESIDUE FROM FLUIDIZED-BED COMBUSTION: ENGINEERING AND LABORATORY STUDIES

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PREFACE

The Westinghouse R&D Center is carrying out a program to provide experimental and engineering support for the development of fluidized-bed combustion systems under contract to the Industrial Environmental Research Laboratory, U. S. Environmental Protection Agency (EPA), at Research Triangle Park, NC. The contract scope includes atmospheric and pressurized fluidized-bed combustion processes as they may be applied for steam generation, electric power generation, or process heat. Specific tasks include work on calcium-based sulfur removal system studies (e.g., sorption kinetics, regeneration, attrition, modeling), alternative sulfur sorbents, nitrogen oxide emissions, particulate emissions and control, trace element emissions and control, spent sorbent and ash disposal, and system evaluation (e.g., the impact of new source performance standards on fluidized-bed combustion system design and cost).

This report contains the results of work defined and completed under the task on environmental control using calcium-based sorbents. The work was carried out from December 1975 to January 1977. Results from work carried out by Westinghouse or reported by other investigators after January 1977 are not assimilated into this task report. The work reported represents an extension of prior work completed by Westinghouse under contract to EPA. Results from this prior work on fluidized-bed combustion include:

- Assimilation of available data on fluidized-bed combustion, including sulfur dioxide removal, sorbent regeneration, sorbent attrition, nitrogen oxide minimization, combustion efficiency, heat transfer, particle carry-over, boiler tube corrosion/erosion fouling, and gas-turbine erosion/corrosion deposition

- Assessment of markets for industrial boilers and utility power systems
- Development of designs for fluidized-bed industrial boilers
- Development of designs for fluidized-bed combustion utility power systems: atmospheric-pressure fluidized-bed combustion boiler-combined cycle power systems, adiabatic fluidized-bed combustion-combined cycle power systems--including first- and second-generation concepts
- Preparation of a preliminary design and cost estimate for a 30 MW (equivalent) pressurized fluidized-bed combustion boiler development plant
- Assessment of the sensitivity of operating and design parameters selected for the base power plant design on plant economics
- Collection of experimental data on sulfur removal and sorbent regeneration using limestone and dolomites
- Preparation of cost and performance estimates for once-through and regenerative sulfur removal systems
- Evaluation of alternative sulfur sorbents
- Collection and analysis of data on spent sorbent disposal--utilization and environmental impact of disposal
- Projection and analysis of trace emissions from fluidized-bed combustion systems
- Analysis of particulate removal requirements and development of a particulate control system for high-temperature, high-pressure fluidized-bed combustion systems
- Construction of a high-pressure/temperature particulate control test facility
- Development of plant operation and control procedures
- Construction of a corrosion/erosion test facility for the 0.63 MW Exxon miniplant
- Continued assessment of fluidized-bed combustion power plant cycles and component designs to evaluate environmental impact.

The results of these surveys, designs, evaluations, and experimental programs provide the basis for the work being carried out under the current contract. Seven reports are available that document the prior contract work (see references 3, 6, 36). Other reports published under the current contract include "Alternatives to Calcium-Based Sorbents for Fluidized-Bed Combustion: Conceptual Evaluation,"(65) "Calcium-Based Sorbent Regeneration for Fluidized-Bed Combustion,"(66) and Evaluation of Trace Element Release from Fluidized-Bed Combustion Systems."(67)

ABSTRACT

An understanding of the environmental impact of the disposal of spent limestones and dolomites and of fuel ash is critical for the success of fluidized-bed combustion (FBC) processes. Land and ocean disposal of unprocessed and processed effluent solids have been studied. The quantity and composition of spent sorbents produced from six reference FBC processes are projected. Effluent solids from atmospheric and pressurized fluidized-bed combustion processes, once-through and regenerated spent sorbent, and bed material and carry-over solids were experimentally investigated. Laboratory testing procedures were developed to determine spent sorbent characteristics, leaching behavior, and thermal activity. Processing the spent sorbent and ash was experimentally investigated to develop alternatives for reducing the environmental impact and to provide alternatives for potential utilization. The environmental impact from the land disposal of unprocessed and processed effluent solids is estimated on the basis of results from an experimental test program and compared with the behavior of natural gypsum and the drinking water standards. The potential for ocean disposal is assessed.

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SECTION 1

INTRODUCTION

Fluidized-bed combustion for electric power generation provides the potential for improved thermal conversion efficiency, reduced costs, and reduced environmental impact when compared with conventional technology. The fluidized-bed combustion process, operated at atmospheric or elevated pressure, typically results in the production of spent bed material in the form of dry, partially utilized dolomite or limestone particles from 0 to 6 mm in size. This spent bed material is referred to in this report as "spent sorbent." In addition, fine particles of sorbent and ash will be collected in the particulate-removal system. This material collected in the flue gas particle control equipment is referred to in this report as "carry-over" or "fly ash," although it includes some sorbent as well as ash. The spent sorbent bed material may be either regenerated for recycling to the fluid-bed boiler for repeated sulfur dioxide removal or disposed of in its partially sulfated form in a once-through system. The former process has the potential advantage of producing less solid waste for disposal. The properties of these spent sorbents (size distribution, composition, etc.) are sensitive to a number of operating and design factors. The major compounds in the waste stone to be disposed of are calcium sulfate, calcium oxide, calcium carbonate, and magnesium oxide when dolomite is used; and calcium sulfate and calcium oxide or calcium carbonate when limestone is used. Trace elements arising from impurities in the coal and sorbent will also be present.

The quantity of spent sorbent will depend upon the amount of fresh sorbent fed - that is, upon the sulfur content of the fuel, the emission standard, the operating conditions, the sorbent characteristics, and whether or not sorbent regeneration is employed. The spent sorbent for disposal will generally range from 0.01 to 0.5 kg sorbent/kg coal. Disposal of the fly ash must also be considered.

An understanding of the environmental impact from the disposal or use of the spent sorbent and fly ash is critical for the successful implementation of fluidized-bed combustion processes. The present program is designed to provide a basis for:

- Projecting environmental impact from disposal
- Interpreting results from large-scale demonstration sites
- Developing optimal system and design and operating requirements, and means for treatment of the residue, to minimize the environmental impact from the spent sorbent and coal ash
- Screening utilization options in view of the environmental impact.

The scope of the program conceived to achieve these objectives includes: identification of fluidized-bed combustion spent sorbent and coal ash characteristics and quantities; development of laboratory tests to quantify the environmental impact for land and ocean disposal; conducting environmental impact tests on actual FBC spent sorbent and ash for land and ocean disposal; studying methods for reducing the impact of the material upon disposal; and performing investigations to identify potential land and ocean utilization options and the resulting potential environmental impact. The work reported represents results from the first 12 months of the current program (December 1975 to December 1976).

SECTION 2

CONCLUSIONS

SPENT SORBENT CHARACTERISTICS

The nominal spent sorbent compositions projected for three basic fluidized-bed combustion concepts are as follows:

Process	Sorbent	$CaSO_4$	Spent Sorbent Composition, mole % (weight %)				
			CaS	CaO	$CaCO_3$	MgO	Balance
Atmospheric Pressure FBC Once-through 100% load	Limestone	25 (43.7)	0 (0)	75 (54)	0 (0)	0^a (0)	1.73^c (2.3)
Pressurized Boiler Once-through 100% load	Dolomite	80 (64.1)	0 (0)	20 (6.6)	0 (0)	1.19^b (28.1)	2.11^c (1.2)
Adiabatic Combustor Once-through 100% load	Dolomite	50 (46.7)	0 (0)	50 (19.2)	0 (0)	1.19^b (32.7)	2.11^c (1.4)
Pressurized Boiler Once-through 100% load	Limestone	40 (60.6)	0 (0)	60 (37.4)	0 (0)	0^a (0)	1.73^c (2)
Atmospheric FBC One-step regeneration 100% load	Limestone	$24^d/12.8^e$ (43.1/26.1)	$0^d/1.2^e$ (0/1.3)	$76^d/86^e$ (54.6/70.1)	0 (0)	0^a (0)	1.73^c (2.3/2.5)
Pressurized Boiler Once-through turndown to minimum load	Dolomite	60 (47.6)	0 (0)	0 (0)	40 (23.4)	1.19^b (27.8)	2.11^c (1.2)

---

[a] MgO included with balance of components

[b] moles MgO/mole Ca

[c] grams per mole calcium

[d] spent sorbent from combustor

[e] spent sorbent from regenerator

The size distribution of spent sorbent from the bed will be similar to the sorbent feed size distribution.

The spent sorbent fines appearing in the fly ash will depend upon sorbent attrition rate, bed elutriation rate, and fines recycle (if applied). The coal ash, in general, will all be elutriated from the combustor. The quantity of sorbent fines is estimated to range from 0.25 to 1 times the coal ash content of the fly ash for a nominal 10 percent ash coal.

SPENT SORBENT/ASH LAND DISPOSAL

Environmental impact criteria have not yet been established for the land disposal of spent sorbent. Leaching and activity tests were developed to permit the projection of environmental impact from land disposal. Criteria for determining the environmental impact of the residue, as well as standardized leaching tests, may be developed separately by EPA in the near future under the Resource Conservation and Recovery Act (PL 94-580).

In the absence of other standards for comparison at the present time, drinking water standards and leachate from a natural gypsum were selected as reference standards for the leachate tests.

Leaching and activity tests were performed on atmospheric and pressurized fluidized-bed combustion systems; once-through and regenerated spent sorbent; bed and carry-over materials; and processed and unprocessed spent sorbent.

Leaching and activity tests show that:

- No water pollution is expected from the leaching of those trace-metal ions for which drinking water standards exist, since the leachate meets drinking water standards.
- An insignificant amount of magnesium is leached out, even for dolomite sorbent.
- Sulfide may not be a problem for the once-through sorbent, since the sulfide concentration in the leachate is below detection limits.

- The total dissolved organics are below detection limits.
- Residual activity, reflected by heat release upon exposure to water, has not been observed to be significant with spent sorbent from once-through pressurized operation. The heat release property of spent sorbent, however, is a function of the FBC operating conditions - for example, temperature, stone residence time, degree of sulfation and calcination, and degree of dead-burning.
- Heat release from the spent sorbent in the atmospheric FBC system is judged an environmental concern for direct disposal. This is due to the large amount of calcium oxide present in the spent sorbent.
- Moderate heat release has occurred with the spent sorbent from the regenerative pressurized FBC system. This, also, may be an environmental concern.
- Potential concerns in the leachates are the high concentrations of calcium, sulfate (SO_4), pH, and total dissolved solids (TDS), which are above drinking water standards.
- The addition of $\geq$20 wt % ash to the spent sorbent improves leachate quality. Codisposal of spent sorbent and ash, thus, can reduce the adverse environmental impact.
- The environmental impact is reduced by room-temperature processing.

A preliminary comparison of environmental impacts is shown in the following chart.

Sample	Process	Sorbent Type	Environmental Parameters							
			Heat Release*-Spontaneous Temp. Rise (3g/20 ml)	Trace Metal	Total Dissolved Solids	Total Organic Carbon	pH	Calcium	Sulfate	Sulfide
Bed Material	Pressurized FBC, once-through	Limestone	<0.2°C		▩		▩	▩	▨	
Bed Material	Pressurized FBC, once-through	Dolomite	<0.2°C		▨		▩	▨	▨	
Bed Material	Pressurized FBC, regenerative	Dolomite	To be determined		▩		▩	▩	▨	To be determined
Bed Material	Atmospheric FBC, once-through	Limestone	To be determined		▩		▩	▩	▨	
Fly Ash	Pressurized FBC, once-through	Limestone	<0.2°C		▨		▩	▨	▨	
Mixture of bed material and fly ash (unprocessed)	Pressurized FBC, once-through	Dolomite/ Limestone	<0.2°C		▨		▩	▨	▨	
Processed Compacts from bed material/ fly ash mixtures	Pressurized FBC, once-through	Dolomite/ Limestone	<0.2°C		▨		▩	▨	▨	
Gypsum	Natural	--	<0.2°C					▨	▨	

*Based on results from limited samples available and subject to the procedures specified in the section on "Activity".

▩ Do not meet either the drinking water or gypsum leachate criteria

▨ Pass gypsum leachate criteria but not drinking water standards

☐ Pass both drinking water and gypsum leachate criteria

SPENT SORBENT UTILIZATION

The construction industry is considered the most attractive market area for utilization because of the need to market large quantities of spent sorbent and the potential demand for waste-based products in construction. Utilization options include landfill, road subbase, aggregate, concrete, and cement.

Integration of basic industries (e.g., a cement plant) with the steam/power plant are potentially attractive for achieving resource and energy conservation.

Test results show that stable, solid compacts can be produced from the spent sorbent and coal ash at ambient temperature and pressure. Compressive strengths meet landfill requirements and may permit substitution for concrete in low-strength applications.

Tests results show pressing of spent sorbent and coal ash results in an axial compressive strength of up to 90 MPa. The compressive strength of Portland cement is 103 to 172 kPa.

OCEAN DISPOSAL/UTILIZATION

EPA policy is to phase out ocean disposal of industrial waste by 1981. Permits for such disposal are unlikely, although research permits may be issued.

The spent sorbent/ash, however, could potentially be utilized as a habitat for marine life.

SECTION 3

RECOMMENDATIONS

SPENT SORBENT CHARACTERISTICS

Obtain spent sorbent from operating test units and demonstration plants to determine characteristics. Compare results with projections. Revise models, as needed, to predict spent sorbent characteristics.

SPENT SORBENT/ASH DISPOSAL

Continue leaching and heat-release tests. These tests should include sorbents generated with the following variations in process parameters:

- Once-through/regenerative sorbent system
- Atmospheric pressure/pressurized combustor
- Limestone/dolomite sorbent
- One-step/two-step regeneration
- Calcium-based sorbent/alternative sorbent
- Wide range of operating conditions within each process variation.

Emphasis should be placed on the environmental impact from the disposal of sorbent produced by a once-through system under atmospheric pressure, since that is the process considered for the first-generation plants.

Extend leaching tests to include pH, temperature, and salinity of leachate-inducing liquid. Extend leachate measurements to include other potential pollutants, according to the EPA comprehensive analysis concept.(1,2)

Perform column-leaching tests to investigate larger amounts of spent sorbent, its permeability, its possible use as landfill, rate of leachate generation, and soil attenuation. A Lysimeter can be designed to simulate actual disposal geometry, seasonal changes, average natural precipitation, and soil composition.

Continue investigation of processing spent sorbent to reduce the residue's environmental impact. Spent sorbent from atmospheric-pressure operation is of particular interest since the heat release of this material may prevent direct disposal.

Perform field tests to monitor ground and surface water and to generate information for commercial projection. The success of a land disposal operation depends greatly on the design, construction, and operation based on the geology, hydrology, topography, and climate of a particular site.

SPENT SORBENT/ASH UTILIZATION

Perform tests to investigate spent sorbent/ash blending to form a compact at ambient temperature/pressure. Perform freeze-thaw and sulfate resistance tests on the fixed compact.

Investigate the effect of spent sorbent composition (e.g., silica, alumina, calcium sulfate) on the low-temperature processing option.

Investigate alternative applications, such as agricultural use.

Develop preliminary process design and economics based on screening tests, for processing options that are attractive.

OCEAN DISPOSAL/UTILIZATION

Implement the marine ecological assessment program to determine deleterious effects of spent sorbent/ash and to conduct flow-through tests with a spent sorbent habitat.

SECTION 4

CHARACTERISTICS OF FBC ASH AND SPENT SORBENT

Fluidized-bed combustion power generation systems, operated at atmospheric pressure and elevated pressures, produce spent sorbent materials (limestone- or dolomite-based) that may require processing to generate a material environmentally suitable for disposal, or to convert them into useful by-products. The properties of these spent sorbents (size distribution, composition, etc.) are sensitive to a number of combustor operating and design factors. The purpose of this study is to project the most probable base characteristics for the spent sorbents that will permit sorbent processing and environmental impact studies to proceed on a meaningful and consistent basis.

Spent sorbent characteristics are projected; and fresh sorbent, coal, and coal ash properties are also discussed. The assumptions and data applied to project the spent sorbent properties are summarized to permit future refinement as new information becomes available. A perspective on the sensitivity of the spent sorbent characteristics to the design and operating conditions and the applied assumptions is also provided.

FACTORS INFLUENCING THE SPENT SORBENT CHARACTERISTICS

The following factors have a significant influence on the characteristics of the spent sorbent produced by the fluidized-bed combustion system:

- Coal properties - sulfur content, heating value, and ash content
- Fresh sorbent properties - type of sorbent (limestone or dolomite), composition, physical structure, and attrition behavior

- Fluid-bed combustion system concept - power cycle (atmospheric-pressure boiler, pressurized boiler, adiabatic combustor), once-through or regenerative operation, and sorbent pretreatment
- Fluid-bed combustor design and operating conditions - temperature, pressure, excess air, residence times of sorbent and gas, calcium-to-sulfur feed ratio, superficial velocity, coal and sorbent feed size, coal and sorbent feeding, internals design, distributor design, turndown operating conditions, and so forth.
- Regeneration process concept - once-step (high-temperature) process or two-step (low-temperature) process, point of fresh sorbent feeding, and point of spent sorbent withdrawal
- Regenerator design and operating conditions - temperature, pressure, reactant-gas (or solid reductant) composition, residence times of sorbent and gas, multiple stages or regions, internals design, distributor design, and superficial velocity, and the like
- Other system components design - particulate control, sorbent circulation, and so forth.

The list is not exhaustive, but the factors presented appear to be the most significant. The following spent sorbent characteristics are considered:

- Composition (major components) - CaO, $CaCO_3$, CaS, $CaSO_4$, MgO, and other components present in fresh sorbent which are retained in the spent sorbent
- Size distribution of bed material and overhead fines.

Projections of the relative amounts of coal ash and spent sorbent are also considered because of their important processing implications. Trace element content of the spent sorbent has not been projected.

Figure 1 is a general sorbent flow diagram for fluidized-bed combustion. A fluid-bed combustor is shown with two stages of particulate control equipment: the first stage represents recycling of coarse sorbent and ash (or carbon) to the combustor, and the second stage represents removal of ash and sorbent fines from the combustor system to be processed or regenerated. The sorbent material to be processed or regenerated then consists of the sorbent stream withdrawn from the combustor, having the bulk bed characteristics, and the sorbent-fines stream withdrawn from the particulate control system. If the operation is once-through, these two streams would represent the spent sorbent.

For the regenerative case another processing step with particulate control is shown in Figure 1. The regenerated sorbent is recycled to the combustor. The spent sorbent is represented by the fine material withdrawn from the combustor and regenerator particulate control systems, plus the sorbent withdrawn either from the combustor or the regenerator bulk beds. In the regenerative case fresh sorbent may be injected into the process in either the combustor or the regenerator. The nature of the spent sorbent may also be sensitive to the exact location within the bulk beds from which it is withdrawn (e.g., near the distributor in an oxidizing region or near the top of the bed in a reducing region).

While all of the factors that can be identified cannot be entirely accounted for, a reasonable projection of the spent sorbent properties in terms of the major factors is possible.

Fresh Sorbent, Coal, and Coal-Ash Properties

Sorbent (limestone and dolomite) compositions were studied in some detail for both fluidized-bed combustion systems and limestone wet-scrubber systems. A summary of compositions for limestone and dolomite is shown in Tables 1 and 2. Limestone 1359 and dolomite 1337 were previously used as bases for fluidized-bed combustion process studies and have the compositions shown in Tables 3 and 4.(3)

Coal compositions were analyzed for a large number of coals from the eastern U. S. Mean values, standard deviations, and minimum and maximum values are given for trace elements, minor and major elements,

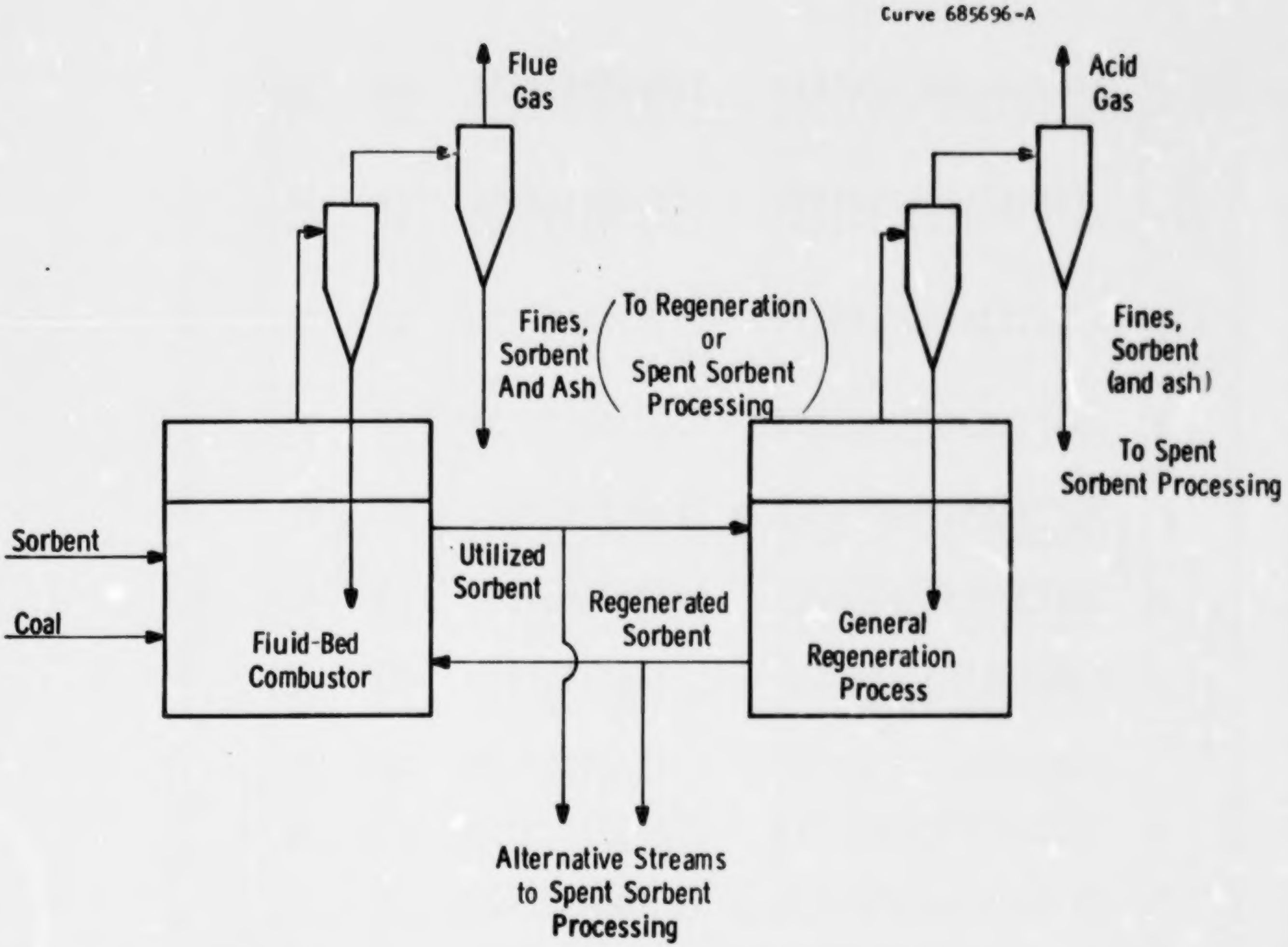
Curve 685696-A
Flue Gas
Acid Gas
Fines, Sorbent And Ash
To Regeneration or Spent Sorbent Processing
Fines, Sorbent (and ash)
To Spent Sorbent Processing
Sorbent
Coal
Utilized Sorbent
Regenerated Sorbent
Fiuid-Bed Combustor
General Regeneration Process
Alternative Streams to Spent Sorbent Processing

Figure 1. Fluidized-Bed Combustion General Sorbent Flow Diagram

TABLE 1. CHEMICAL AND MINERALOGICAL PROPERTIES OF LIMESTONES

Sorb. Type	Ign. loss	Composition wt %[(a)]							Grain Size, coded[(c)]	Unit-cell Length a, Å	Crystal-lite Size, μ
		CaO	MgO	Fe_2O_3	Na_2O	K_2O	MnO_2	Gangue[(b)]			
					Calcites						
1336	43.2	53.4	1.5	0.2	0.0057	0.0284	0.0085	1.6	3.0	4.978	0.149
1343	42.5	54.1	0.5	0.4	0.0115	0.0575	0.0345	0.7	1.0	4.989	0.167
1350	43.6	54.7	0.5	0.2	0.0056	0.0282	0.0451	2.6	2.0	4.986	0.177
1355	33.1	41.5	1.2	1.6	0.2542	0.4349	0.0268	24.6	1.0	4.982	0.024
1359	43.6	54.7	0.7	0.1	0.0056	0.0282	0.0141	0.9	1.0	4.985	0.124
1363	36.1	42.2	0.9	1.6	0.1406	0.6518	0.1278	18.0	1.0	4.989	0.124
1368	40.1	49.1	1.3	0.9	0.0898	0.2636	0.9165	8.8	2.6	4.978	0.097
1369	43.4	54.3	0.8	0.1	0.0396	0.0736	0.0085	0.8	1.0	4.987	0.127
1377	27.3	28.4	2.8	5.1	0.2326	3.9985	0.0872	43.8	1.0	4.975	0.162
1379	41.3	48.7	2.2	0.4	0.1526	0.2818	0.0411	6.6	3.0	4.930	0.097
1677	26.5	31.2	1.1	0.7	0.0735	0.2058	0.0110	45.0	1.0	4.987	0.177
1679	42.7	52.1	1.4	0.3	0.0917	0.0802	0.0086	3.6	1.0	4.975	0.048
1681	37.7	44.9	2.2	0.6	0.0623	0.2056	0.0093	13.8	1.0	4.985	0.115
1685	43.9	48.2	4.6	0.4	0.0505	0.0280	0.0617	3.0	2.8	4.986	0.145
1687	43.2	53.4	1.2	0.1	0.0284	0.0363	0.0284	1.5	2.6	4.986	0.177
1691	38.6	47.3	1.7	0.6	0.0860	0.3438	0.0430	12.4	1.0	4.984	0.107
1692	42.9	54.8	0.3	0.1	0.0255	0.0286	0.0086	0.6	3.0	4.985	0.186
1693	42.7	53.3	0.6	0.2	0.0573	0.1031	0.0086	2.8	1.0	4.985	0.160
					Dolomites						
1337	47.2	29.0	22.7	0.2	0.0053	0.0264	0.0079	1.0	2.0	4.811	0.119
1340	46.2	30.7	19.9	1.4	0.0054	0.0269	0.6890	2.0	1.5	4.808	0.141
1341	46.7	29.8	22.4	0.3	0.0053	0.0266	0.0080	0.7	3.0	4.806	0.211
1367	43.9	32.5	15.8	5.2	0.0224	0.0280	0.5610	7.0	1.0	4.816	0.085
1380	46.7	30.4	21.9	0.3	0.0266	0.0266	0.0080	0.6	2.5	4.805	0.189
1678	30.8	19.7	14.5	1.3	0.0830	0.9826	0.0415	35.0	1.5	4.808	0.141
1680	42.4	28.2	19.3	0.9	0.0346	0.2534	0.0691	9.2	1.0	4.806	0.171
1686	46.9	29.7	22.0	0.2	0.0159	0.0266	0.0080	1.0	3.0	4.806	0.189
1688	47.1	29.1	22.2	0.5	0.0159	0.0265	0.0159	0.5	1.5	4.807	0.182
1690	34.0	22.4	15.5	1.1	0.0396	1.1286	0.0792	24.2	3.0	4.809	0.098
1695	42.2	28.9	23.1	0.6	0.0289	0.0289	0.0087	4.8	3.0	4.808	0.189
1701	42.5	34.5	13.5	4.3	0.0920	0.1553	0.4542	8.6	1.3	4.822	0.090
1702	44.6	33.2	18.0	0.8	0.0277	0.2715	0.0083	4.6	1.3	4.810	0.070
					Mixtures						
1360	44.5	45.0	7.2	0.7	0.0277	0.0277	0.0888	3.4	2.5	4.910	0.135
1694	38.0	37.2	12.4	0.6	0.0310	0.0310	0.0093	12.6	3.0	4.886	0.159
					Magnesites						
1375	46.4	15.8	32.2	0.9	0.0322	0.1340	0.0080	10.0	2.5	4.720	0.147
1376	48.8	7.1	41.0	0.8	0.0154	0.0256	0.0154	28.0	2.5	4.720	0.220

(a) Calculated from composition of calcine.
(b) Accessory minerals.
(c) 1 x fine, <63 μ; 2 = medium, 63-250 μ; 3 = coarse, >250 μ.
*Reproduced from "Investigation of the Reactivities of Limestone to Remove Sulfur Dioxide from Flue Gas," TVA, 1971, PB 202-407.

TABLE 2. ACCESSORY MINERAL CONTENT OF LIMESTONES*

Sorb. Type	Total	Accessory minerals (wt %)								
		Quartz	Illite	Montmor-illonite	Chert	Tremo-lite	Limo-nite	Feld-spar	Musco-vite	Glass frit
					Calcites					
1336	1.6	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
1343	0.7	0.3	0.1	0.0	0.2	0.0	0.1	0.0	0.0	0.0
1350	2.6	1.6	0.9	0.0	0.0	0.0	0.1	0.0	0.0	0.0
1355	24.6	16.0	8.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1359	0.9	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.4
1363	18.0	6.0	6.0	0.0	0.0	0.0	0.0	0.0	6.0	0.0
1368	8.8	4.2	4.2	0.0	0.0	0.0	0.4	0.0	0.0	0.0
1369	0.8	0.4	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1377	43.8	13.1	13.1	0.0	0.0	0.0	4.5	0.0	13.1	0.0
1379	6.6	4.6	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0
1677	45.0	14.0	0.0	14.0	0.0	0.0	3.0	0.0	0.0	14.0
1679	3.6	1.7	1.7	0.0	0.0	0.0	0.2	0.0	0.0	0.0
1681	13.8	4.6	4.6	0.0	4.6	0.0	0.0	0.0	0.0	0.0
1685	3.0	1.0	1.0	0.0	0.9	0.0	0.1	0.0	0.0	0.0
1687	1.5	0.5	0.5	0.0	0.4	0.0	0.0	0.0	0.0	0.1
1691	12.4	3.8	8.0	0.0	0.0	0.0	0.6	0.0	0.0	0.0
1692	0.6	0.3	0.2	0.0	0.0	0.0	0.1	0.0	0.0	0.0
1693	2.8	1.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
					Dolomites					
1337	1.0	0.7	0.0	0.2	0.0	0.0	0.1	0.0	0.0	0.0
1340	2.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1341	0.7	0.0	0.0	0.0	0.0	0.5	0.0	0.1	0.0	0.0
1367	7.0	0.3	0.0	0.0	0.0	0.0	6.7	0.0	0.0	0.0
1380	0.6	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.3
1678	35.0	15.7	15.7	0.0	0.0	0.0	1.8	1.8	0.0	0.0
1680	9.2	3.1	0.0	0.0	0.0	0.0	0.0	3.1	0.0	3.0
1686	1.0	0.3	0.3	0.0	0.3	0.0	0.0	0.0	0.0	0.0
1688	0.5	0.2	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.1
1690	24.2	20.6	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1695	4.8	1.4	0.5	0.0	0.0	1.4	0.0	0.0	1.4	0.0
1701	8.6	3.0	0.0	0.0	0.0	0.0	5.6	0.0	0.0	0.0
1702	4.6	2.3	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
					Mixtures					
1360	3.4	0.0	0.4	0.0	1.3	0.0	1.3	0.0	0.0	0.4
1694	12.6	4.0	0.0	0.0	0.0	4.0	0.0	0.0	0.6	0.0
					Magnesites					
1375	10.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1376	28.0	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

*Reproduced from "Investigation of the Reactivities of Limestone to Remove Sulfur Dioxide from Flue Gas," TVA, 1971, PB 202-407.

TABLE 3. ANALYSIS OF LIMESTONE NO. 1359

Component	As-Received, wt %(4)
SiO_2	0.85
Al_2O_3	0.30
Fe_2O_3	0.17
MgO	1.07
CaO	97.
TiO_2	<0.05
SrO	0.07
Na_2O	<0.02
K_2O	<0.1
MnO_2	<0.05

TABLE 4. SO_2 SORBENT ANALYSIS USED FOR PRELIMINARY FLUIDIZED-BED BOILER ANALYSES

Component	As-Received(4) Dolomite 1337, wt %
SiO_2	0.78
Al_2O_3	0.15
Fe_2O_3	0.25
MgO	45.0
CaO	53.0
TiO_2	0.02
SrO	<0.03
Na_2O	<0.02
K_2O	<0.1
MnO_2	<0.03

total sulfur and ash in Table 5. The variability of coal compositions is very great for almost all components. An Ohio-Pittsburgh No. 8 Seam coal was previously used as the basis for fluidized-bed combustion process studies.(3) Its composition and the associated ash composition are shown in Table 6.

Expected coal and fresh sorbent size distributions are presented in Figure 2.(3) The size distribution is typical of that obtained from commercial crushers. Although finer sizes or narrower size distributions may have possible process advantages, they require pulverization and/or more extensive size classification.

Plant Sulfur Balances

The required sulfur removal efficiency for the total fluidized-bed combustion power plant is determined by the existing SO_x emission standard for coal-fired power plants and is given by the following expression:

$$1 - \varepsilon_S = \frac{SH}{W_S \; 2 \times 10^6} , \qquad (1)$$

where ε_S is the plant sulfur removal efficiency, S is the SO_x emission standard in kg SO_2/GJ, W_S is the coal sulfur content (weight fraction), and H is the coal heating value. This relationship is illustrated in Figure 3 for an emission standard of 0.516 kg SO_2/GJ which corresponds to the present U.S. EPA standard for large coal-fired boilers. Two coal heating values, which span the range of typical values, are considered.

The sulfur removal efficiency required in the fluidized-bed combustor is dependent upon the sulfur removal or recovery efficiencies of the individual processing systems comprising the power plant sulfur removal system (i.e., the regeneration system, the sulfur recovery system and the spent sorbent processing system) and the process logic applied to the sulfur removal system (i.e., once-through versus regenerative operation, recycle of tail-gases to the fluid-bed combustor or the sulfur recovery process, withdrawal of spent sorbent before or after the regeneration step, etc.).

TABLE 5. MEAN ANALYTICAL VALUES FOR ALL 101 COALS*

Constituent	Mean	Std	Min.	Max.
As	14.02 ppm	17.70	0.50	93.00
B	102.21 ppm	54.65	5.00	224.00
Be	1.61 ppm	0.82	0.20	4.00
Br	15.42 ppm	5.92	4.00	52.00
Cd	2.52 ppm	7.60	0.10	65.00
Co	9.57 ppm	7.26	1.00	43.00
Cr	13.75 ppm	7.26	4.00	54.00
Cu	15.16 ppm	8.12	5.00	46.00
F	60.94 ppm	20.99	25.00	143.00
Ga	3.12 ppm	1.06	1.10	7.50
Ge	6.59 ppm	6.71	1.00	43.00
Hg	0.20 ppm	0.20	0.02	1.60
Mn	49.40 ppm	40.15	6.00	181.00
Mo	7.54 ppm	5.96	1.00	30.00
Ni	21.07 ppm	12.35	3.00	80.00
P	71.10 ppm	72.81	5.00	400.00
Pb	34.78 ppm	43.69	4.00	218.00
Sb	1.26 ppm	1.32	0.20	8.90
Se	2.08 ppm	1.10	0.45	7.70
Sn	4.79 ppm	6.15	1.00	51.00
V	32.71 ppm	12.03	11.00	76.00
Zn	272.29 ppm	694.23	6.00	5350.00
Zr	72.46 ppm	57.78	8.00	133.00
Al	1.29 %	0.45	0.43	3.04
Ca	0.77 %	0.55	0.05	2.67
Cl	0.14 %	0.14	0.01	0.54
Fe	1.92 %	0.79	0.34	4.32
K	0.16 %	0.06	0.02	0.43
Mg	0.05 %	0.04	0.01	0.25
Na	0.05 %	0.04	0.00	0.20
Si	2.49 %	0.80	0.58	6.09
Ti	0.07 %	0.02	0.02	0.15
ORS	1.41 %	0.65	0.31	3.09
PYS	1.76 %	0.86	0.06	3.78
SUS	0.10 %	0.19	0.01	1.06
TOS	3.27 %	1.35	0.42	6.47
SXRF	2.91 %	1.24	0.54	5.40
ADL	7.70 %	3.47	1.40	16.70
Mois.	9.05 %	5.05	0.01	20.70
Vol	39.70 %	4.27	18.90	52.70
FIXC	48.82 %	4.95	34.60	65.40
Ash	11.44 %	2.89	2.20	25.80
Btu/lb	12748.91	464.50	11562.00	14362.00
C	70.28 %	3.87	55.23	80.14
H	4.95 %	0.31	4.03	5.79
N	1.30 %	0.22	0.78	1.84
O	8.68 %	2.44	4.15	16.03
HTA	11.41 %	2.95	3.28	25.85
LTA	15.28 %	4.04	3.82	31.70

Note: Abbreviations other than standard chemical symbols: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (Mois), volatile matter (Vol), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

*Reproduced from "Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," R. R. Ruch, H. J. Gluskoter, N. F. Shimp, 1974, EPA-650/2-74-054 (Reference 5).

TABLE 6. OHIO PITTSBURGH NO. 8 SEAM COAL*

SAMPLE:	Run of mine - as received	
PROXIMATE ANALYSIS (wt %):	Moisture	3.3
	Volatile matter	39.5
	Fixed carbon	48.7
	Ash	8.5
		100.0
ULTIMATE ANALYSIS (wt %): (includes moisture)	C	71.2
	H	5.4
	O	9.3
	N	1.3
	S	4.3 (∼60% organic & ∼40% pyritic)
	Ash	8.5
		100.0
GROSS HEATING VALUE:	30,238 J/g	
NET HEATING VALUE:	29,075 J/g	
ASH ANALYSIS (wt %):	SiO_2	45.3
	Al_2O_3	21.2
	Fe_2O_3	27.3
	TiO_2	1.0
	P_2O_5	0.11
	CaO	1.9
	MgO	0.6
	Na_2O	0.2
	K_2O	1.8
	SO_3	0.7
		100.1
FUSIBILITY OF ASH:	Initial deformation temperature	1138°C
	Softening temperature	1221°C
	Fluid temperature	1327°C
PARTICLE DENSITY:	Coal - ∼1.4 g/cc	
	Ash - ∼2.8 g/cc	
GRINDABILITY (Hardgrove):	50-60	
FREE SWELLING INDEX:	5-5.5	

*(Source of data: USBM, Pittsburgh, PA.)

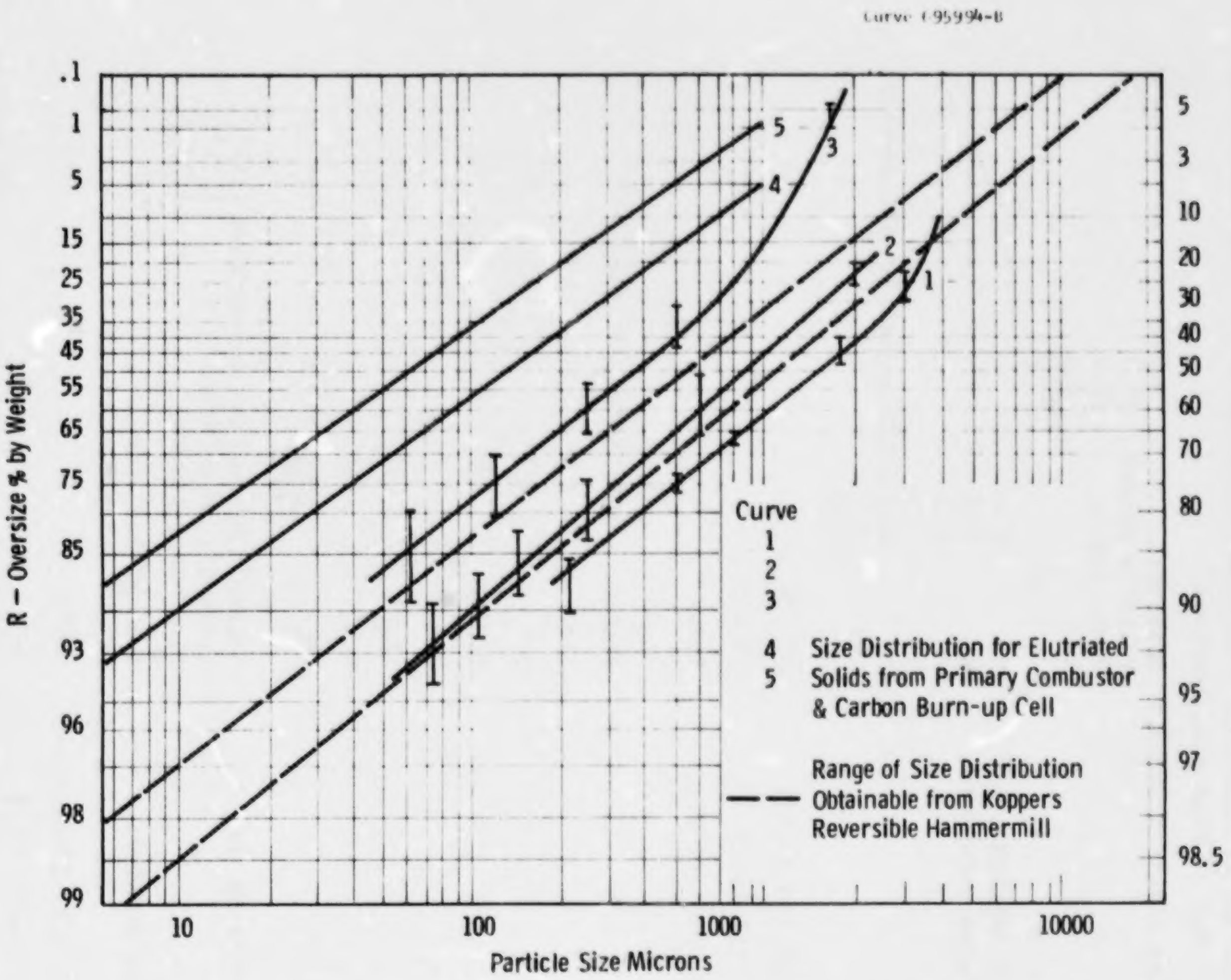

Figure 2. Size Distribution of Coal Feed

Curve 684848-A

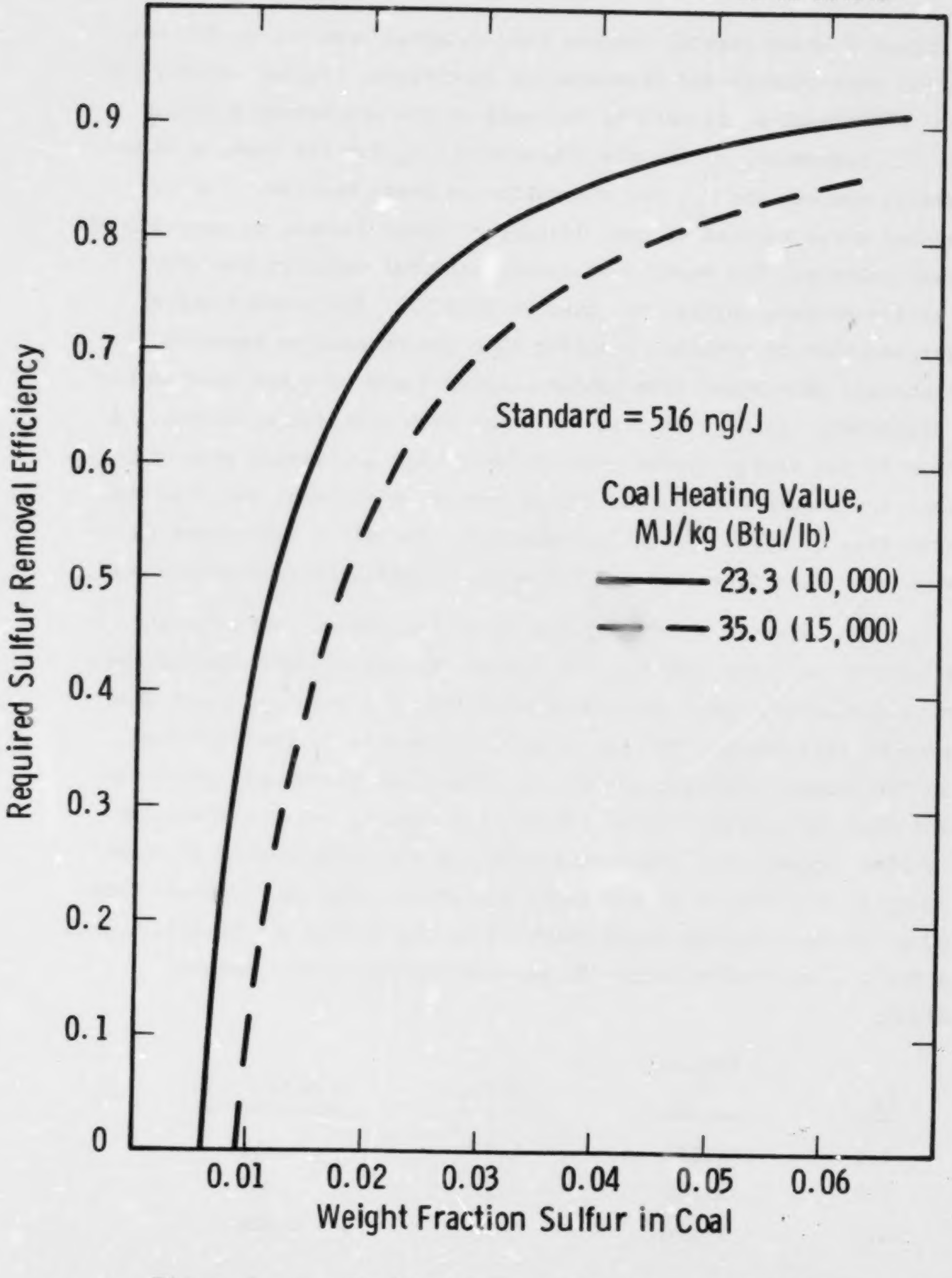

Figure 3. Required Combustor Sulfur Removal Efficiency

Figure 4 shows general process flow diagrams used for sulfur balances for once-through and regenerative operations. Sulfur recovery or removal efficiencies are defined for each of the processing systems: ε_C for the combustor, ε_R for the regenerator, ε_P for the spent sorbent processing system, and ε_{SR} for the sulfur recovery process. Sulfur losses may occur because of gas, liquid, or fines losses, or intentional tail-gas release. The results of simple material balances for some alternative process logics are shown in Table 7. The possibility of the introduction of additional sulfur into the process by means of reductant-gas generation from sulfur-bearing fuels or other sources has been neglected, but in come cases it could be a significant factor. A decrease in the sulfur removal efficiency of any processing step will increase the required combustor sulfur removal efficiency and also the required rate of fresh sorbent consumption. Recycling tail-gases to the combustor also increases the "effective" sulfur content of the coal.

From the relation shown in Table 7, it is evident that, for the cases with no tail-gas recycle, the sulfur removal efficiencies of the separate processing steps must be greater than the required plant sulfur removal efficiency. For the cases with recycle to the combustor, the sulfur removal efficiencies of the individual processing steps can be less than the overall sulfur removal efficiency, but the effective coal sulfur content will increase greatly as the efficiencies decrease. For example, the case of once-through operation, with the tail-gas from the spent sorbent process being recycled to the combustor, is illustrated below for a 5 wt % sulfur coal (85 percent overall sulfur removal required):

ε_P	Required ε_C	W_S^E/W_S	M/M (ε_P = 1)
0.9	0.863	1.094	1.111
0.8	0.876	1.21	1.247
0.7	0.890	1.36	0.424

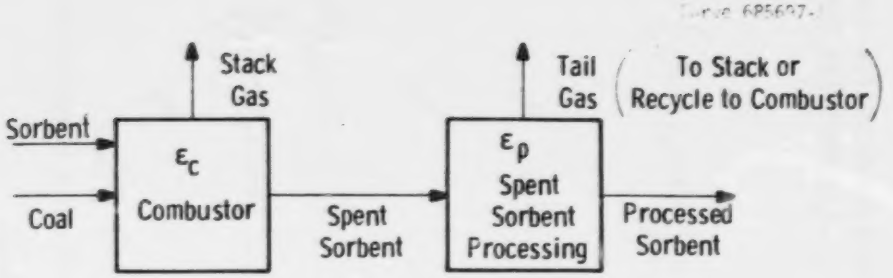
Curve 6P5697-
Stack Gas
Tail Gas
To Stack or Recycle to Combustor
Sorbent
Coal
ε_c
Combustor
Spent Sorbent
ε_p
Spent Sorbent Processing
Processed Sorbent

Figure 4A. General Once-through Operation Sulfur Balances

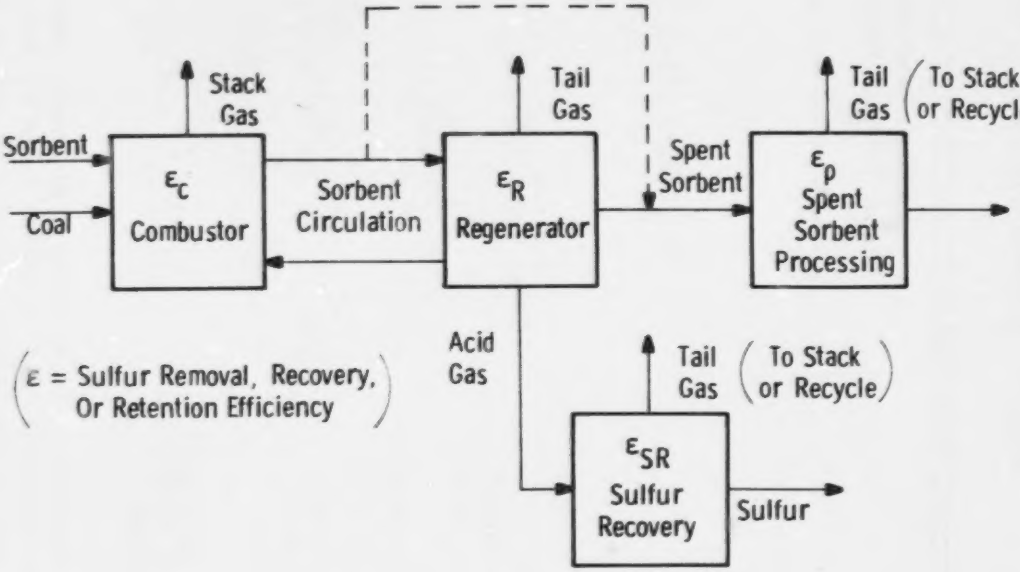
Stack Gas
Tail Gas
Tail Gas
To Stack or Recycle
Sorbent
Coal
ε_c
Combustor
Sorbent Circulation
ε_R
Regenerator
Spent Sorbent
ε_p
Spent Sorbent Processing
Acid Gas
Tail Gas
To Stack or Recycle
ε_{SR}
Sulfur Recovery
Sulfur
(ε = Sulfur Removal, Recovery, Or Retention Efficiency)

Figure 4B. General Regenerative Operation Sulfur Balances

TABLE 7. PLANT SULFUR BALANCE RELATION

Operation	Required Combustor Sulfur Removal Efficiency ε_C	Effective Sulfur Content of Combustor Coal
Once-through		
Tail-gas exhausted	$\varepsilon_S/\varepsilon_P$	W_S
Tail-gas recycled to combustor	$\varepsilon_S\left\{1-(1-\varepsilon_S)(1-\varepsilon_P)\right\}^{-1}$	$W_S\left\{1-(1-\varepsilon_S)(1-\varepsilon_P)\right\}\varepsilon_P^{-1}$
Regenerative		
Tail-gas exhausted; spent sorbent withdrawn after regeneration step	$\varepsilon_S\varepsilon_R^{-1}\varepsilon_{SR}^{-1} + M\bar{U}_R\varepsilon_R^{-1}(1-\varepsilon_P\varepsilon_{SR}^{-1})$	W_S
Tail-gas exhausted; spent sorbent withdrawn before regeneration step	$\varepsilon_S\varepsilon_R^{-1}\varepsilon_{SR}^{-1} + M\bar{U}_C(1-\varepsilon_P\varepsilon_R^{-1}\varepsilon_{SR}^{-1})$	W_S
Sulfur recovery tail-gas recycled to combustor; spent sorbent after regeneration	$\left[\varepsilon_S\varepsilon_R^{-1} + M\bar{U}_R(\varepsilon_{SR}-\varepsilon_P)\varepsilon_R^{-1}\right]\left[1-M\bar{U}_R(1-\varepsilon_{SR}) -(1-\varepsilon_{SR})\left\{1-\varepsilon_S-M\bar{U}_R(1-\varepsilon_P)\right\}\right]^{-1}$	$W_S\left\{1-(1-\varepsilon_{SR})M\bar{U}_R\right\}\left\{1-\varepsilon_C\varepsilon_R(1-\varepsilon_{SR})\right\}^{-1}$
Sorbent processing tail-gas recycled to sulfur recovery process; spent sorbent after regenerator	$\varepsilon_S\varepsilon_R^{-1}\varepsilon_{SR}^{-1} - M\bar{U}_R\varepsilon_P(1-\varepsilon_{SR})$	W_S

ε = Sulfur removal, recovery, or retention efficiency; subscript C = combustor, R = regenerator, P = spent sorbent processing, SR = sulfur recovery process.

$\underline{M}$ = Sorbent makeup rate, moles calcium per mole of sulfur fed in combustor coal.

$\bar{U}$ = Sorbent utilization; subscript R = after regeneration, subscript C = after combustor.

W_S = Wt. fraction of sulfur in coal.

where W_S^E is the effective coal sulfur content. If the sulfur removal efficiency of the spent sorbent processing system drops to 70 percent, the coal has an effective sulfur content 36 percent greater than its actual content, and the sorbent consumption rate must increase by about 43 percent, compared to the case of 100 percent sulfur removal efficiency for the spent sorbent processing system.

The purpose of this discussion is only to point out the complex nature of the system. Projections of sorbent consumption rates based solely on laboratory performance could easily differ from the ultimate commercial performance by as much as a factor of two.

PROJECTION OF SPENT SORBENT AND COAL ASH PRODUCTION RATES

A plant material balance shows in general that the mass of coal ash per unit mass of spent sorbent calcium, A, is given by

$$A = 0.8 \frac{\alpha}{W_S M} , \qquad (2)$$

where α is the mass fraction of ash in the coal, W_S is the coal sulfur mass fraction, and M is the molar makeup rate of sorbent, moles of calcium per mole of sulfur fed.

For a once-through operation

$$M = \varepsilon_C/\overline{U}_C , \qquad (3)$$

where ε_C is the required combustor sulfur removal efficiency and $\overline{U}_C$ is the sorbent utilization obtained in the combustor. The sorbent utilization is a function of the sorbent properties, the combustor operating conditions, and the combustor design. If it is assumed that the spent sorbent processing scheme has a high sulfur efficiency, so that sulfur losses from it can be neglected, then $\varepsilon_C = \varepsilon_S$ as in equation 1, and

$$A = 0.8 \frac{\alpha \overline{U}_C}{W_S} \left\{ 1 - \frac{S \Delta H}{W_S \; 2 \times 10^6} \right\}^{-1} . \qquad (4)$$

The quantity $A/(\alpha\overline{U}_C)$ is shown in Figure 5 as a function of the coal sulfur content. The value of α may range between 0.02 and 0.30 for eastern coals. For once-through operation $\overline{U}_C$ is expected to range between 0.20 and 0.90. Thus, the ratio A (mass ratio of ash to spent sorbent calcium) may range between about 0.1 and 200 for once-through operation.

For regenerative operation the sorbent makeup rate is a function not only of the combustor design and operating conditions, but also of the regenerator design and operating conditions. It is a function of the required combustor sulfur removal efficiency and the other process variables that are not yet well understood. The sorbent attrition behavior may be the controlling factor in many cases where the rate of sorbent deactivation is low. For regenerative operation M may range between 0.2 and 2.0, and the ash/sorbent ratio may range between about 0.15 and 150, a range not much different from the once-through case.

Sorbent Utilization for Once-through Operation

The ranges of sorbent utilization (fraction of calcium as $CaSO_4$ or CaS) to be expected from a once-through fluidized-bed combustor can be projected from the results of Thermogravimetric (TG) experiments. These results have generally agreed with batch fluidized-bed and continuous operation (Exxon miniplant) results. Table 8 lists projections for 500 μm sorbent particle diameters and 90 percent sulfur removal efficiency, based upon the TG results. Three fluidized-bed combustion systems are considered: the atmospheric-pressure boiler, the pressurized boiler (at high and low excess air rates), and the adiabatic combustor. In all three of these systems calcining conditions are expected to prevail (except, possibly, with the pressurized boiler at turndown). Both limestones and dolomites are considered as general classes of sorbents, though performance will differ within these general classes.

For continuous once-through operation a distribution of sorbent utilization will exist in the spent sorbent. If the kinetics of desulfurization are first-order with respect to the SO_2 concentration and

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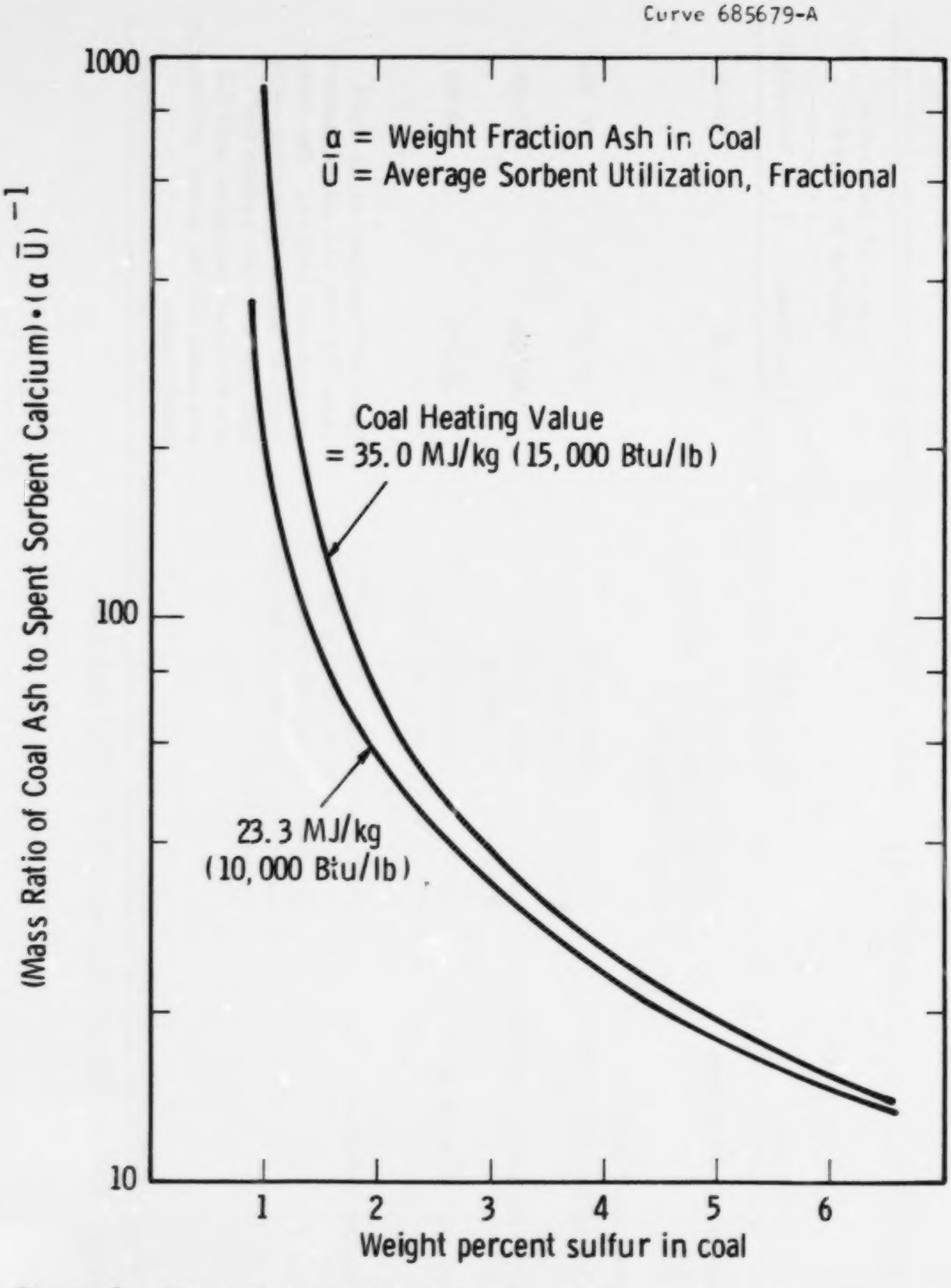

Figure 5. Ratio of Ash to Spent Sorbent for Once-through Operation

TABLE 8. PROJECTIONS OF ONCE-THROUGH SORBENT UTILIZATION*

System	Conditions	Percent of Available Calcium Utilized	
		Limestone	Dolomites
Atmospheric-Pressure Boiler	100 kPa, 815–870°C 10–25% excess air, 15–13% CO_2, calcining	25–35	30–40
Pressurized Boiler			
Low excess air (10%)	1000 kPa, 900–1000°C 15% CO_2, calcining	40–50	80–90
High excess air (100%)	1000 kPa, 900–1000°C, 8.5% CO_2, calcining	40–50	80–90
Adiabatic Combustor	1000 kPa, 900–1000°C, 300% excess air, 4% CO_2, calcining	40–50	50–80
Boiler turndown	Temperature down to ∿750°C, carbonating condition in the pressurized boiler case, calcining conditions in the other cases	Same utilization as at full capacity for all cases except pressurized boiler. For pressurized boiler limestone will not react under carbonated conditions; dolomite will be utilized 50–70% under carbonated conditions.	

*Basis: 500 μm particle diameter, 90% sulfur removal.

the unreacted sorbent concentration, and if the fluidized-bed combustor is perfectly mixed, then it can be shown that the sorbent utilization is distributed as follows:

$$F(U < X) = 1 - (1 - X)^{\left(\frac{1}{\overline{U}} - 1\right)} , \qquad (5)$$

where $F(U < X)$ is the fraction of the spent sorbent having a utilization less than X, and $\overline{U}$ is the average spent sorbent utilization. This result is also independent of the distribution of sulfur releases within the fluidized-bed combustor. The once-through distribution of sorbent utilization is plotted in Figure 6 for average utilizations ranging from 0.1 to 0.9. This distribution should be a reasonable approximation to be applied in cases where the processing or utilization of the spent sorbent is sensitive to its composition distribution.

The sorbent particle size also influences the degree to which it can be utilized in a once-through operation. Figure 7 illustrates this influence.(6) The projections in Table 8 should be reasonable for average particle diameters up to about 1000 μm; larger particle sizes will require a reduction in the projection of the maximum sorbent utilization.

Sorbent Regenerability

Two sorbent regeneration schemes have been considered for fluidized-bed combustion: the one-step, high-temperature regeneration and the two-step, low-temperature regeneration. Two factors of importance to the characterization of the spent sorbents from these regenerative processes are the required makeup rate of fresh sorbent for maintenance of the combustor desulfurization efficiency, and the level of utilization of the sorbent in the combustor and regenerator.

The level of utilization of sorbent in the combustor would be less than the maximum utilizations projected for once-through operation in Table 8. For the projection of the sorbent total sulfur content before

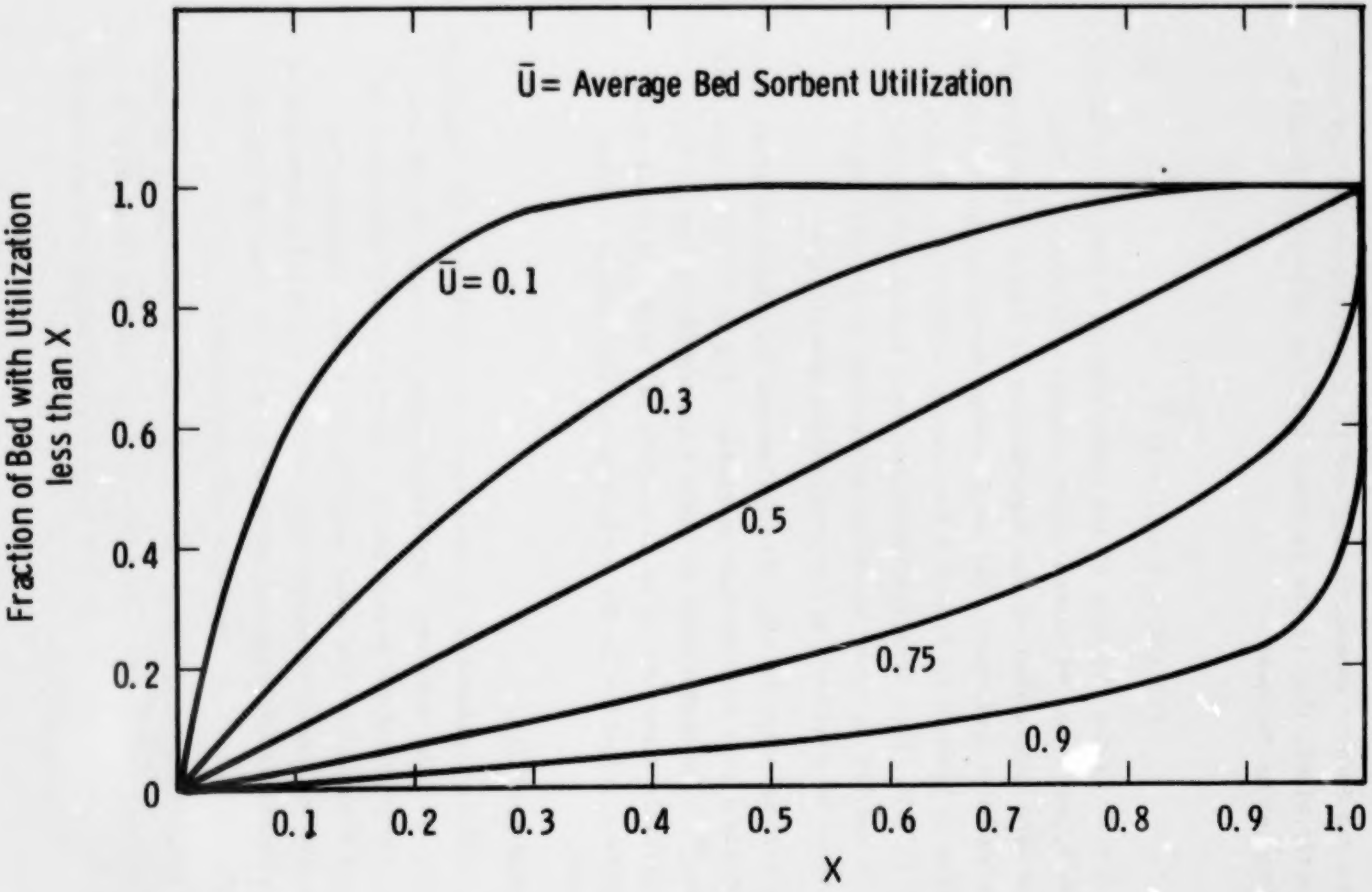

Figure 6. Cumulative Distribution of Sorbent Utilization

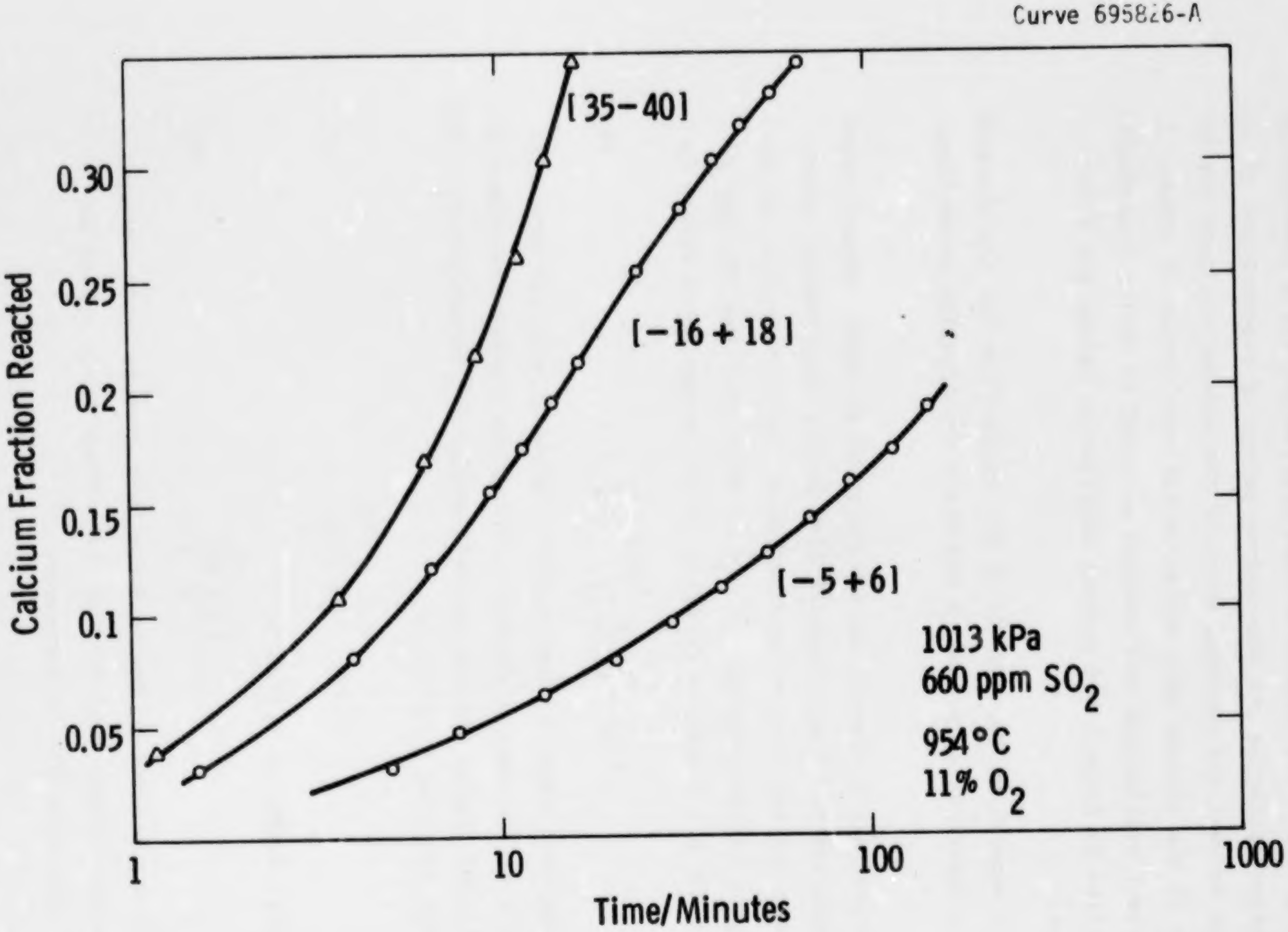

Figure 7. Sulfation of Fully Calcined Tymochtee Dolomite

and after regeneration, the following basis is applied and is illustrated in Figure 8: The maximum sorbent utilization for a once-through desulfurization operation and the maximum extent of regeneration of the once-through sorbent are averaged to yield the assumed ultimate sorbent utilization if the process were cycled an infinite number of times. A typical sorbent utilization differential as found in cyclic experiments is then applied to project the sorbent utilization before and after regeneration.

Table 9 summarizes the results of the projections for the one-step and two-step regeneration processes and lists the specific assumptions applied.

In a regenerative process the distribution of spent sorbent composition is expected to be much broader than in the once-through cases. This statement follows from an examination of the distribution of the number of spent sorbent cycles. It can be shown that the fraction of particles in the spent sorbent residing in the system for n cycles is

$$F(n) = \left(\frac{S}{M + S}\right)^{n-1} \frac{M}{M + S} \quad , \qquad (6)$$

where M is the feed rate of fresh sorbent (moles calcium per mole sulfur fed) and S is the rate of sorbent circulation between the regenerator and combustor (moles calcium per mole sulfur fed to combustor). The cumulative distribution is given by

$$F(n>X) = \left(\frac{S}{M + S}\right)^{X} \quad , \qquad (7)$$

and the average number of cycles is

$$\bar{n} = \left(\frac{M + S}{M}\right) \quad . \qquad (8)$$

Equation 6 is represented in Figure 9 for four average cycle numbers. The distribution becomes very flat as the average cycle number is increased or the ratio M/S is decreased.

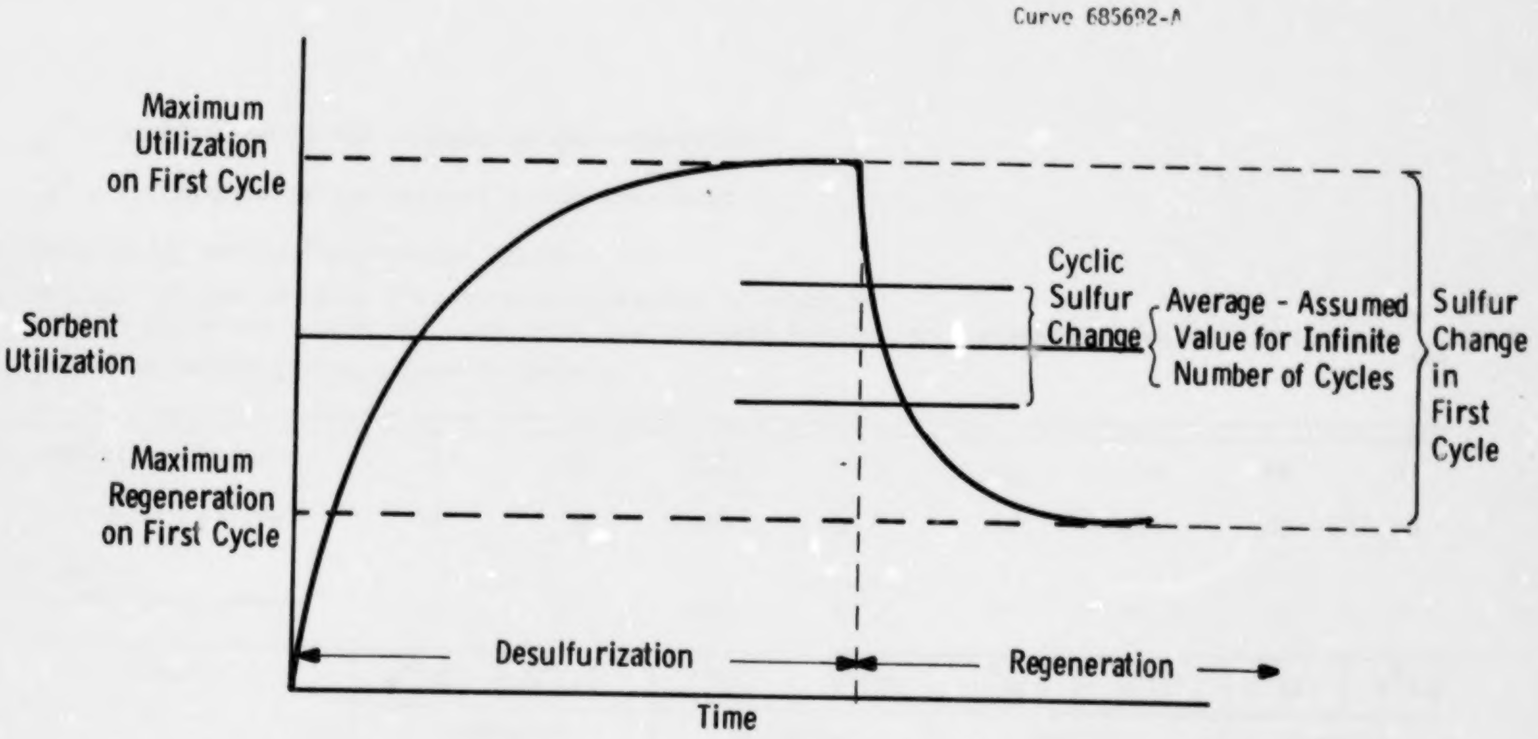

Figure 8. Basis for Regenerative Sorbent Utilization Projection

TABLE 9. PROJECTED REGENERATIVE SORBENT UTILIZATIONS[a]

System	One-Step Regeneration One-Step Regeneration (at combustor pressure)				Two-Step Regeneration			
	Limestone		Dolomite		Limestone		Dolomite	
	U_C(%)[b]	U_R(%)[c]	U_C(%)	U_R(%)	U_C(%)	U_R(%)	U_C(%)	R_R(%)
Atmospheric-Pressure Boiler	24	14	21.5	11.5	--	--	--	--
Pressurized Boiler	35	25	49	39	39	29	73	63
Adiabatic Combustor	35	25	32.5	22.5	39	29	48	38

[a] Based on values (lower) given in Table 8.

Assumes 50% regeneration on first cycle for one-step process with limestone and 90% for dolomite(7) and 30% for the two-step process with limestone or dolomite.

Assumed 10% sorbent utilization differential.

[b] U_C = utilization of the sorbent in the combustor.

[c] U_R = utilization of the sorbent in the regenerator.

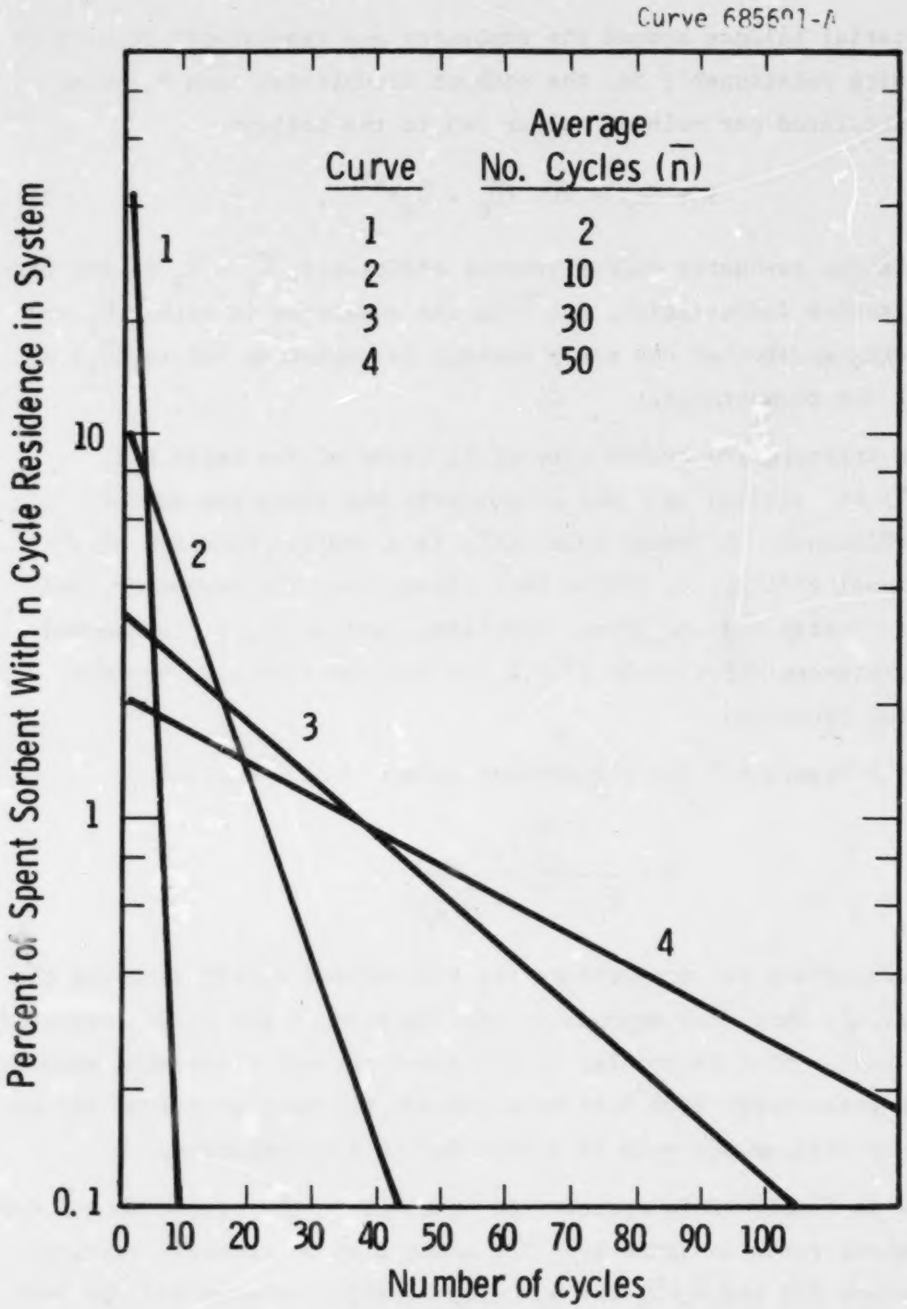

Figure 9. Distribution of Cycle Number for Regenerative Spent Sorbent

A material balance around the combustor and regenerator results in the following relationship for the sorbent circulation rate S, moles of calcium circulated per mole of sulfur fed to the boiler:

$$S = (\varepsilon_C - M\overline{U})\ (\overline{U}_C - \overline{U}_R)^{-1}\ , \qquad (9)$$

where ε_C is the combustor sulfur removal efficiency, $\overline{U}_C - \overline{U}_R$ is the sorbent utilization differential, and $\overline{U}$ in the numerator is either $\overline{U}_C$ or $\overline{U}_R$, depending on whether the spent sorbent is withdrawn before $(\overline{U}_C)$ or after $(\overline{U}_R)$ the regenerator.

For a regenerative system a specific value of the ratio M/S ($\equiv 1/(\overline{n}-1)$) is required in order to maintain the combustor sulfur removal efficiency. Although this ratio is a complex function of the sulfur removal efficiency, the sorbent properties, the combustor, and regenerator design and operating conditions, and so on, it is assumed to have a representative value of 0.1 for the one-step and two-step regeneration processes.

Solving Equation 9 for the sorbent makeup rate M yields:

$$M = \frac{\left(\frac{M}{S}\right)\varepsilon_C}{\overline{U}_C - \overline{U}_R + \overline{U}\left(\frac{M}{S}\right)}\ .$$

Table 10 summarizes the projections for the sorbent makeup rate and the quantity $M\overline{U}/\varepsilon_C$, which corresponds to the fraction of the sulfur captured in the combustor that is handled by the spent sorbent processing system. The makeup rates range from 0.49 mole calcium per mole of sulfur fed to 0.75 mole of calcium per mole of sulfur fed to the combustor.

There is considerable speculation involved in the projection of the sorbent makeup rates in Table 10. The assumption of constant value of the parameters M/S and $\overline{U}_C$-$\overline{U}_R$ for both regeneration schemes and for both limestone and dolomite sorbents is certainly an oversimplification. It was also shown in Table 7 that the required combustor sulfur removal

TABLE 10. PROJECTED SORBENT MAKEUP RATES[a]

System	One-step Regeneration								Two-Step Regeneration							
	Limestone				Dolomite				Limestone				Dolomite			
	A[b]		B[c]		A		B		A		B		A		B	
	M^d	$M\bar{U}/\epsilon_C^{e,f,g}$	M	$M\bar{U}/\epsilon_C$	M	$M\bar{U}/\epsilon_C$	M	$M\bar{U}/\epsilon_C$	M	$M\bar{U}/\epsilon_C$	M	$M\bar{U}/\epsilon_C$	M	$M\bar{U}/\epsilon_C$	M	$M\bar{U}/\epsilon_C$
Atmospheric-Pressure Boiler	0.69	0.20	0.75	0.12	0.70	0.18	0.76	0.10	--	--	--	--	--	--	--	--
Pressurized Boiler	0.63	0.26	0.68	0.20	0.57	0.33	0.61	0.28	0.61	0.28	0.66	0.23	0.49	0.42	0.52	0.39
Adiabatic Combustor	0.63	0.26	0.68	0.20	0.64	0.25	0.69	0.18	0.61	0.28	0.66	0.23	0.57	0.32	0.62	0.28

[a] Basis: $\epsilon_C = 0.85$, $M/S = 0.1$ (equivalent to $\bar{n} = 11$), $\bar{U}_C - \bar{U}_R = 0.1$

$$M = \frac{\frac{M}{S}\epsilon_C}{\bar{U}_C - \bar{U}_R + \bar{U}\frac{M}{S}}$$

[b] A - withdrawal of spent sorbent before regeneration step ($\bar{U}-\bar{U}_C$)

[c] B - withdrawal of spent sorbent after regeneration step ($\bar{U}-\bar{U}_R$)

[d] M - sorbent make-up rate, moles of calcium per mole of sulfur

[e] U - sorbent utilization, subscript C = after combustor, R = after regenerator; no subscript means either C or R depending on the point of spent sorbent withdrawal.

[f] ϵ_C - combustor sulfur removal efficiency, fractional.

[g] $M\bar{U}/\epsilon_C$ represents the fraction of the captured sulfur handled by the spent sorbent process.

efficiency and the effective sulfur content of the coal may vary greatly, depending upon the sulfur efficiency of the sulfur removal system subsystems and the choice of tail-gas recycle or tail-gas cleaning.

Sorbent Attrition and Elutriation

The previous projections in this report have assumed that sorbent attrition losses are negligible when compared to those of sorbent deactivation. This may not be a valid assumption in all cases, and in some instances the sorbent makeup rate may be determined by the sorbent attrition losses rather than by the sorbent activity losses. When sorbent attrition is the controlling factor for the sorbent makeup, it is expected that a substantial stream of spent sorbent will be generated in the form of fines (probably <100 μm diameter) having compositions significantly different from those previously projected.

The rate of particle attrition and elutriation in a commercial fluidized-bed combustion power plant will be very sensitive to the operating conditions, the sorbent properties, and the hardware design: sorbent feeders, distributor plates, bed internals, cyclones, pneumatic transport systems, and so on. Experimental work conducted to address attrition has not sufficiently characterized the phenomena to permit a meaningful projection of the rate of sorbent fines generation, the coal ash content of the sorbent fines, and the chemical composition of the sorbent fines.

In general, two stages of particulate control equipment will collect elutriated sorbent and coal ash. Coarse material will be collected in the first stage and recycled to the combustor. The second-stage equipment will trap the fine material. This fine material would probably not be recycled to the combustion because the fines content of the bed and the resulting elutriation and/or fines recycle rate would increase to extreme levels. The sulfur content of the sorbent fines depends upon their residence time in the desulfurizer and the rate of reaction of the fine particles.

While the rate of fines generation and the composition of these fines cannot be projected with any confidence, it is almost certain that some significant stream of sorbent fines will be produced and must be accounted for in the spent sorbent characterization. The following assumptions are applied to determine the spent sorbent fines properties:

- Fines (<100 μm) are captured in the second-stage particulate control equipment at a rate of 10 percent of the sorbent makeup rate.
- Most (95 percent) of the coal ash is captured in the second-stage particulate control equipment.
- Negligible losses of fines occur in the regenerator and in the combustor due to the regenerated sorbent recycle stream (i.e., this stream is attrition resistant).
- The fines composition is equal to the bulk bed composition.

ASSESSMENT OF SPENT SORBENT PROJECTIONS FOR FLUIDIZED-BED COMBUSTION

The basis for the fluidized-bed combustion power plant spent sorbent characterization is summarized in Table 11. Tables 12 through 14 list the spent sorbent projections for once-through operation and for the one-step and two-step regeneration processes. Table 15 considers the spent sorbent produced during plant turndown. Fresh sorbent makeup rates (calcium-to-sulfur mole ratio), rates of sorbent fines (<100 μm), capture from the combustor particulate control equipment (calcium-to-sulfur mole ratio), and the spent sorbent compositions are presented.

The spent sorbent size distribution (coarse bed material) will be similar to the sorbent feed size distribution given in Figure 2, with the amount of modification dependent upon the sorbent attrition rate, the fines recycle rate, and the bed elutriation rate. The sorbent fines size distribution will be similar to curve 4 in Figure 10, depending upon the fines recycle rate, the bed attrition behavior, and the cyclone particle capture performance. Sorbent elutriation from the regenerator vessel has been neglected.

The projections will be updated as new information is developed.

TABLE 11. POWER PLANT BASIS FOR SPENT SORBENT PROJECTIONS

Plant Size = 600 MW_e

Plant Heat Rate - MJ/kWh (Btu/kWh) based on HHV

Atmospheric-pressure boiler	10.08	(9550)(3)
Pressurized boiler	9.50	(8967)(3)
Adiabatic combustor	9.60	(9096)(6)

Coal (Ohio-Pittsburgh No. 8 Seam coal - Table 6)

Sulfur - 4.3 wt %
Ash - 8.5 wt %
Heating value - 29.1 MJ/kg (12,500 Btu/lb) LHV

Coal Rate - Mg/hr

Atmospheric-pressure boiler	200.0	(220.4)
Pressurized boiler	187.7	(206.9)
Adiabatic combustor	190.4	(209.9)

Sulfur Removal Efficiency (%) - no recycle of tail-gases

Power plant - 82.6
Once-through combustor - 87 (assumes $\varepsilon_P = 0.95$ in Table 7)
Regenerative combustor - 92 (assumes, $\varepsilon_P = \varepsilon_R = 1.0$, $\varepsilon_{SR} = 0.90$, Table 7)

Ash in Overhead Fines - 95%
Ash in Coarse Spent Sorbent - 5%

Sorbent Fines Rate - 10% of sorbent makeup rate

Limestone Type - 1359 (Table 3)

Dolomite Type - 1337 (Table 4)

TABLE 12. ONCE-THROUGH SORBENT OPERATION PROJECTIONS

	Sorbent Rate (Ca/S)	Sorbent Fines Rate (Ca/S)	Composition of Spent Sorbent on a Molar-Calcium Basis, Mole % (Total wt fractions in parentheses)						
			$CaSO_4$	CaS	CaO	$CaCO_3$	MgO modes MgO (per mole Ca)	Other Components (gm per mole Ca	Ratio of Wt of Ash to Wt of Spent Sorbent Fines
Atmospheric-Pressure Boiler									
Limestone (1359)	3.48	0.35	25 (0.437)	0 (0)	75 (0.540)	0 (0)	0[a] (0)	1.73 (0.023)	2.46
Dolomite (1337)	2.9	0.29	30 (0.315)	0 (0)	70 (0.302)	0 (0)	1.19 (0.367)	2.11 (0.016)	1.77
Pressurized Boiler									
Limestone (1359)	2.18	0.22	40 (0.606)	0 (0)	60 (0.374)	0 (0)	0[a] (0)	1.73 (0.020)	3.41
Dolomite (1337)	1.09	0.11	80 (0.641)	0 (0)	20 (0.066)	0 (0)	1.19 (0.281)	2.11 (0.012)	3.60
Adiabatic Combustor									
Limestone (1359)	2.18	0.22	40 (0.606)	0 (0)	60 (0.374)	0 (0)	0[a] (0)	1.73 (0.020)	3.41
Dolomite (1337)	1.74	0.17	50 (0.467)	0 (0)	50 (0.192)	0 (0)	1.19 (0.327)	2.11 (0.014)	2.62

(a) MgO is included in other components in the limestone cases.

TABLE 13. ONE-STEP REGENERATION PROJECTIONS

	Sorbent Rate (Ca/S)	Sorbent Fines Rate (Ca/S)	Composition of Spent Sorbent, (Mole %)					
			$CaSO_4$	$CaS^{(a)}$	CaO	$CaCO_3$	MgO (moles MgO per mole Ca)	Other Components (g per mole calcium)
Atmospheric Pressure								
• Limestone								
Combustor	0.75	0.08	24	0	76	0	0	1.73
Regenerator	0.81	0.08	12.8	1.2	86	0		
• Dolomite								
Combustor	0.76	0.08	21.5	0	78.5	0	1.19	2.11
Regenerator	0.82	0.08	10.4	1.1	88.5	0		
Pressurized Boiler								
• Limestone								
Combustor	0.68	0.07	35	0	65	0	0	1.73
Regenerator	0.74	0.07	21.5	3.5	75	0		
• Dolomite								
Combustor	0.62	0.06	49	0	51	0	1.19	2.11
Regenerator	0.66	0.07	34.1	4.9	61	0		
Adiabatic Combustor								
• Limestone								
Combustor	0.68	0.07	35	0	65	0	0	1.73
Regenerator	0.74	0.07	21.5	3.5	75	0		
• Dolomite								
Combustor	0.69	0.07	32.5	0	67.5	0	1.19	2.11
Regenerator	0.75	0.08	19.2	3.3	77.5	0		

(a) 5% of the $CaSO_4$ converted to CaS in atmospheric-pressure case, 10% conversion to CaS in pressurized case.

TABLE 14. TWO-STEP REGENERATION PROJECTIONS

	Sorbent Rate (Ca/S)	Sorbent Fines Rate (Ca/S)	Composition of Spent Sorbent (Mole %)					
			$CaSO_4$ (a)	CaS (b)	CaO	$CaCO_3$ (c)	MgO (moles MgO per mole Ca)	Other Components (g per mole calcium)
Pressurized Boiler								
• Limestone								
Combustor	0.66	0.07	18.7	20.3	6.1	0	0	1.73
Regenerator	0.71	0.07	0	29	46.7	21.3		
• Dolomite								
Combustor	0.53	0.05	73	0	27	0	1.19	2.11
Regenerator	0.56	0.06	0	63	25.9	11.1		
Adiabatic Combustor								
• Limestone								
Combustor	0.66	0.07	18.7	20.3	61	0	0	1.73
Regenerator	0.71	0.07	0	29	46.7	21.3		
• Dolomite								
Combustor	0.62	0.06	48	0	52	0	1.19	2.11
Regenerator	0.67	0.07	0	38	43.4	18.6		

(a) 30% of limestone-based-sorbent CaS resulfated in combustor; 100% of dolomite-based sorbent resulfated in combustor

(b) 100% conversion of $CaSO_4$ to CaS in first step

(c) 100% calcination in combustor; 30% conversion of CaO to $CaCO_3$ in second step.

TABLE 15. TURNDOWN SPENT SORBENT PROJECTS

	Sorbent Rate (Ca/S)	Composition of Spent Sorbent on a Molar-Calcium Basis Mole % (Total Weight Fractions in Parentheses)					
		$CaSO_4$	CaS	CaO	$CaCO_3$	MgO (moles MgO per mole Ca)	Other Components (g per mole calcium)
Pressurized Boiler							
Dolomite (1337)	1.45	60 (0.476)	0 (0)	0 (0)	40 (0.234)	1.19 (0.278)	2.11 (0.012)

Assumptions:

- All processes operated once-through during turndown.
- Dolomite-based processes operate at about 750°C during turndown for pressurized operation.
- Limestone-based processes operate at turndown such that calcining conditions always occur in the combustor.
- All other cases (other than the pressurized boiler with dolomite) result in compositions identical to those in Table 12 (i.e., the calcium-to-sulfur ratio is fixed during turndown and the sorbent performance is not affected by turndown conditions).

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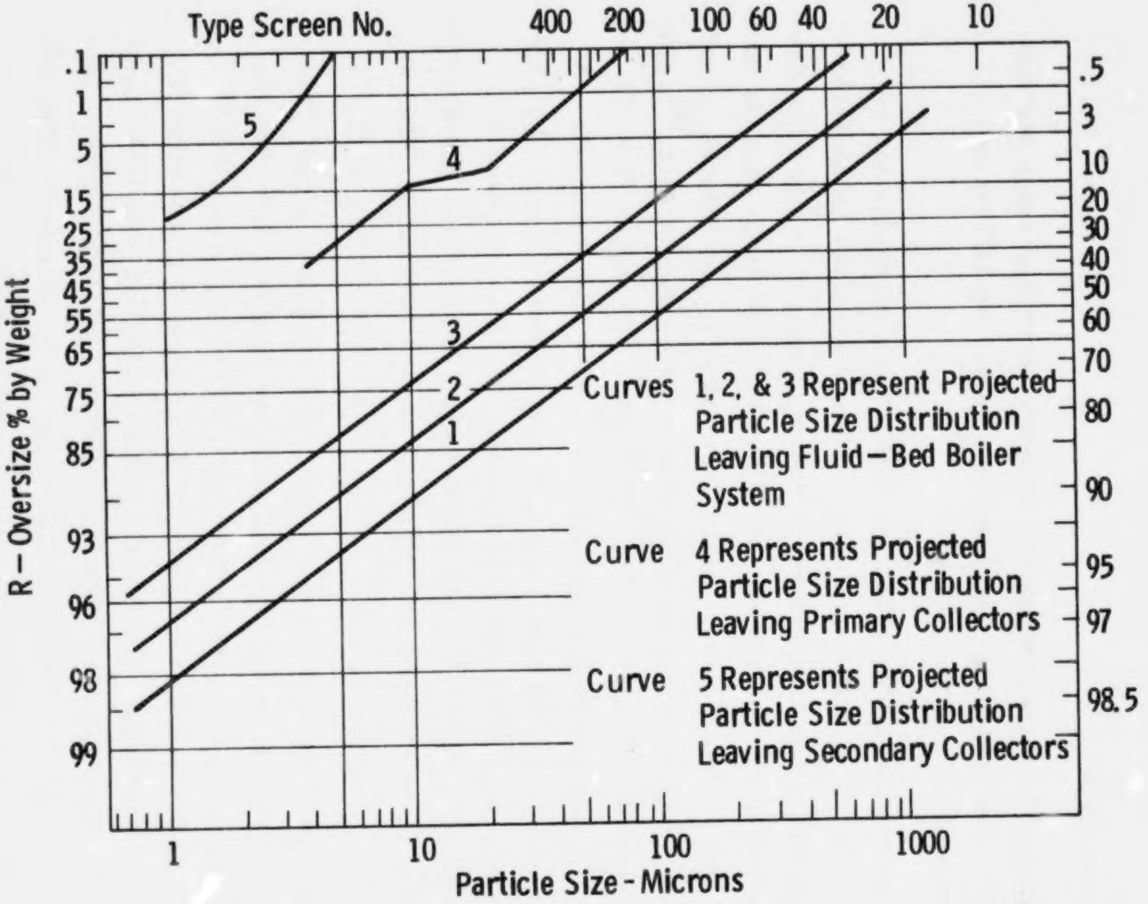

Figure 10. Particle Size Distribution for Different Gas Streams

SECTION 5

LAND DISPOSAL

REGULATIONS/CRITERIA

The legislative developments and criteria governing spent sorbent disposal have been reviewed. The important laws, regulations and criteria are summarized in this section.

With the enactment of the National Environmental Policy Act of 1969 (NEPA), all of us are charged with a "responsibility to contribute to the preservation and enhancement of the environment." Since the disposal of the solid wastes from the fluidized-bed combustion process must satisfy the provisions of environmental regulations, the federal legislative developments governing liquid discharges from power plants,(8) disposal of dredged and fill materials,(9,10) water discharges from all sources,(11,12) and landfill practices(13,14) have been reviewed. These include three of the most important environmental laws: The Clean Air Act Amendments of 1970; the Federal Water Pollution Control Act (Public Law 92-500, 1972);(14) and the Resource Conservation and Recovery Act (The Solid Waste Disposal Act of 1965, Public Law 89-272, 1965, as amended by Public Law 91-512, 1970 and by Public Law 94-580, 1976).

Although environmental standards for solid residue disposal from coal-fired boilers (including the fluidized-bed systems) have not yet been promulgated, the Resource Conservation and Recovery Act (RCRA) requires EPA to set criteria by April 1978 for identifying whether a solid waste is considered "hazardous," and to establish standards covering generation, handling, treatment, and disposal of such wastes. If the residue were not "hazardous" -- and there is no indication that the FBC residue would be at this time -- it would be subject to any restrictions developed by the individual states under their respective management plans within the guidelines established by EPA as required by the RCRA.

In anticipation of forthcoming criteria for solid waste disposal and the quality of its leachate, the chemical characteristics of leachates from leaching experiments are compared with the drinking water standards given by the EPA National Interim Primary Drinking Water Regulations (NIPDWR),(16) The United States Public Health Service (USPHS)(17) Drinking Water Standards, and the World Health Organization (WHO) Potable Water Standards.(18) This is, of course, extremely conservative; a leachate dilution/attenuation factor of 10 is currently being considered in the regulation draft under Section 3001 of the RCRA of 1976 by the Hazardous Waste Management Division of the Office of Solid Waste, EPA. It must be pointed out that the drinking water standards are used in this investigation only in an effort to put data into perspective in the absence of EPA guidelines and should not be construed as suggesting that the leachate must necessarily meet drinking water standards. Although the guidelines for the power plant effluents are not applicable to the disposal of dry spent sorbent from the fluidized-bed combustion process, they are used as additional references in this investigation.

Because of the wide variations in the characteristics of solid wastes, in general, weather, soils, topography, groundwater from site to site, and nearby stream quality and flow characteristics, permits are currently being awarded on a site-specific basis. Eventually, as a result of RCRA, state regulations will apply, but these regulations will not be enacted until federal standards are enacted. Depending on the actual site selected for the spent sorbent disposal, the leachates would have to meet the water quality criteria for the specific water use.(19) The success of a land disposal application depends, furthermore, above all, on the design, construction, and operation for a specific disposal site based on the geology, hydrology, and climate of that particular site.

Related Literature on Disposal

The solid waste research program, under the leadership of EPA, initially concentrated on programs associated with municipal solid wastes, but recently has included studies on hazardous and industrial wastes in anticipation of new regulations and standards for hazardous and nonhazardous industrial wastes.(20,21) Abundant literature is available on sanitary landfill and pollutant migration from municipal wastes.(20-25) Recent work includes studies on land disposal of solid wastes from flue gas cleaning systems with emphasis on flue gas desulfurization sludges.(20,26-29)

Literature on disposition of spent sorbent from fluidized-bed coal combustion is limited but includes BCURA(30) and PER,(31) who conducted bench-scale leaching on small numbers of sorbents with results that basically agreed with the findings from the present investigation. Argonne National Laboratory(32) investigated the marketability of spent limestone or dolomite from fluidized-bed combustion for agricultural and structural uses and found it potentially feasible. Under contract to EPA, Ralph Stone and Company(33,34) recently joined EPA's fluidized-bed combustion program on the task of environmental assessment of residues from fluidized-bed combustion of coal and gasification of high-sulfur fuel oils. TVA,(35) under interagency agreement with EPA, is expanding its original studies on disposal or recycle of sludges from lime/limestone wet-scrubbing processes to include work on characterization and disposition of the waste products from the fluidized-bed combustion process.

In addition to the preliminary environmental assessment(36) based on experimental results using actual spent sorbent from Argonne's pressurized fluidized-bed combustor, Westinghouse conducted similar studies on spent sorbent from the high-temperature fluidized-bed gasification process,(36,37) which employs dry granular calcium-based sorbent for sulfur removal.

TABLE 16. SELECTED WATER QUALITY CRITERIA

Substance	Maximum Concentrations (mg/ℓ)			
	National Interim Primary Drinking Water Regulations(16)	PHS Regulations on Drinking Water(15)	World Health Organization Potable Water Standards(18)	Proposed Guidelines for Power Plant Effluent(8)
pH (pH unit)			7 - 8.5	6.0 - 9.0
Total dissolved solids		500	500	
Ag	0.05	0.05		
As	0.05	0.05	0.2	
Ba	1.0	1.0		
Ca			75	
Cd	0.01	0.01		
Cr	0.05	$1.0(Cr^{+3})$ $0.05(Cr^{+6})$	0.05	0.2
Cu		1.0	1.0	1.0
Fe		0.3	0.3	1.0
Hg	0.002			
Mg			50	
Mn		0.05	0.1	
Ni		2.0		
Pb	0.05	0.05	0.1	
Se	0.01	0.01	0.05	
Sn		1.0		
SO_4		250	200	
Zn		5.0	5.0	1.0

EXPERIMENTAL TESTING PROGRAM

The environmental impact of any disposed material is a function of its physical and chemical properties as well as of the quantity involved. Potential water pollution problems can be predicted from the chemical characteristics of leachates such as pH, specific ion concentrations, trace element dissolution, and total dissolved solids. Disposal of the solid wastes from the fluidized-bed coal combustion process may also create air pollution, odor nuisance, and heat-release problems. To assess the environmental impact of solid waste disposal and the suitability of waste material as landfill, leaching and activity tests were performed on actual spent sorbents and fly ash obtained from the fluidized-bed combustors operated by Argonne National Laboratory,(32) Exxon Research and Engineering CCompany,(38) and Pope, Evans and Robbins (PER),(31) all of whom are conducting studies on the fluidized-bed coal combustion process under contracts to EPA or DOE. The spent sorbents available for this study include spent bed material and fly ash from both the pressurized and atmospheric-pressure boilers operated with a once-through or regenerative sorbent system.

Samples

Batches of actual spent sorbent and fly ash from pilot-scale fluidized-bed combustors tested for their environmental impact on disposal are listed below:

- Argonne spent sorbent from run C2/C3 — from Argonne's 15-cm pressurized fluidized-bed combustion unit(32)
- Argonne once-through spent sorbent from run VAR-4
- Argonne once-through spent sorbent from run LST-1
- Argonne once-through spent sorbent from run LST-2
- Argonne once-through spent sorbent from run LST-3
- Argonne once-through spent sorbent from run LST-4
- Argonne regenerative spent sorbent from run REC-3 — third combustion experiment in 10-cycle combustion/regeneration series of experiments

- Argonne regenerative spent sorbent from run CCS-10 — tenth regeneration experiment in 10-cycle combustion/regeneration series of experiments
- Exxon spent sorbent from run 8.4 — from Exxon's 32-cm pressurized fluidized-bed combustion unit, i.e., Exxon miniplant in Linden, New Jersey(38)
- Exxon spent sorbent from run27
- Exxon fly ash from run 27
- Exxon spent sorbent from run 19.6
- Exxon fly ash from run 19.6
- Exxon spent sorbent from run 30.2
- Exxon fly ash from run 26
- Exxon fines from run 34
- PER sorbent -- from Pope, Evans and Robbins's atmospheric-pressure fluidized-bed combustor of 0.46 x 1.83 m size
- Gypsum — ground Iowa gypsum 114 was used to represent a reference for natural $CaSO_4$ leachability.

Processed compacts of Exxon No. 27 spent sorbent/fly ash mixture by room-temperature blending (see Section 7 for Compact Preparation) include the following:

- I1C and I1D -- 35.8 wt % fly ash, 7 day air cure
- I2C and I2D -- 35.8 wt % fly ash, 11 day air cure
- I3C and I3D -- 35.8 wt % fly ash, 28 day air cure
- II1C and II1D -- 10 wt % fly ash, 7 day air cure
- II4C and II4D -- 10 wt % fly ash, 52 day air cure.

Table 17 summarizes the process conditions under which these sorbents are generated. For the purpose of clarification, the term "spent sorbent" refers to the bed material, "fly ash" to the carry-over material collected in the primary particulate control device (cyclones), and "fines" represents the very fine particulates that have passed the cyclones and are collected on an additional filter or flue gas sampling device.

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TABLE 17. PROCESS CONDITIONS OF SAMPLES STUDIED FOR THEIR ENVIRONMENTAL IMPACT ON DISPOSAL

Conditions \ Samples	Argonne C2/C3	Argonne VAR-4	Argonne[(a)] REC-3	Argonne[(b)] CCS-10	Argonne LST-1	Argonne LST-2	Argonne LST-3	Argonne LST-4
Coal	Arkwright	Arkwright	Arkwright	Triangle	Arkwright	Arkwright	Arkwright	Arkwright
Sorbent	Tymochtee dolomite	Tymochtee dolomite	Tymochtee dolomite	Tymochtee dolomite	Limestone 2203	Dolomite 1337	Dolomite 1351	Limestone 1336
Run Length (hr)	23	11	80.6	2.6	34.7	25.5	18.4	17.5
Pressure (kPa)	810	810	810	152	810	810	810	810
Avg Bed Temp (°C)	900–955	900	900	1100	870	870	870	870
Lower Bed Temp (°C)	—	—	—	—	—	—	—	—
Gas Velocity (m/s)	1.61–1.67	0.7	0.7	1.24	0.76	0.76	0.76	0.76
Expanded Bed Height (m)	—	0.91	0.91	0.46	0.91	0.91	0.91	0.91
Settled Bed Height (m)	—	—	—	—	—	—	—	—
Coal Feed Rate (kg/hr)	—	7.9	13.5	—	12.1	11.7	11.7	11.6
Sorbent Feed Rate (kg/hr)	—	2.6	2.9	—	1.7	3.6	3.1	1.5
Ca/S Molor Ratio	1.1–1.5	1.9	1.5	—	1.5	1.8	1.4	1.4
Excess Air	—	17	17	Reducing	17	17	17	17
SO_2 Emission (ppm)	80–375	122	450	67,000	900	160	270	990
NO_x (ppm)	135	185	120	—	150	135	185	95
CO (ppm)	—	50	64	—	74	50	30	55
CO_2 (%)	—	18	16	—	16	15	16	17
O_2 (%)	3.0	3.0	3.2	—	3.5	3.1	2.9	3.0
S Retention (%)	82–96	95	79	~65% Regeneration	63	93	89	58
lb SO_2/MBtu	—	0.23	0.85	—	1.5	0.28	0.47	1.7
lb NO_2/MBtu	—	0.25	0.16	—	0.18	0.17	0.23	0.12

(a) Third combustion experiment in ten-cycle combustion/regeneration series of experiments

(b) Tenth regeneration experiment in ten-cycle combustion/regeneration series of experiments

TABLE 17. (Cont'd)

Conditions / Samples	Exxon 8.4	Exxon 27	Exxon 19.6	Exxon 30.2	Exxon 26	Exxon 34	PER
Coal	Arkwright	Champion	Champion	Champion	Champion	Champion	Sewickley
Sorbent	Grove limestone 1359	Pfizer dolomite 1337	Grove limestone 1359	Grove limestone 1359	Grove limestone 1359	Pfizer dolomite 1337	Grove limestone
Run Length (hr)	11	240	7.5	8.5	15.5	13.25	--
Pressure (kPa)	906-907	930	930	920	930	932	101.3
Avg Bed Temp (°C)	—	829-930	880-888	929	885-927	900	816°C
Lower Bed Temp (°C)	877-908	840-960	—	945	949	868	—
Gas Velocity (m/s)	1.77-1.83	1.7-2.2	2.01-2.04	2.5	1.9-2.1	1.5	2.7-4.6
Expanded Bed Height (m)	—	3-7	—	--	—	--	—
Settled Bed Height (m)	0.66-1.19	—	1.58	--	1.12-2.28	2.29	0.3-0.9
Coal Feed Rate (kg/hr)	75-112	112-149	113-143	137	130	90	272-363
Sorbent Feed Rate (kg/hr)	10.3-15.2	—	—	--	--	--	0-182
Ca/S Molar Ratio	1.67	0-2.5	2.5	3.7	3.7	0.75	--
Excess Air	18-72	8-23	15	17.2	9.5-11.5	20.9	—
SO$_2$ Emission (ppm)	--	20-1290	500	137	140-300	100-300	--
NO$_x$ (ppm)	50-200	70-210	104	--	180-185	52	--
CO (ppm)	--	30-110	--	45	50	61	—
CO$_2$ (%)	--	1.1-17	11.7-12.3	15.1	13	15.5	--
O$_2$ (%)	--	1.5-3.9	2.5-3.0	3.1	1.8-2.15	3.5	3
S Retention (%)	62	41-100	69	89	81-91	--	—
lb SO$_2$/MBtu	1.8	0.03-2.5	1.0	--	0.29-0.59	--	—
lb NO$_2$/MBtu	--	0.12-0.30	0.14	—	0.25-0.28	--	--

Spent Sorbent Characterization

Chemical and physical characterization of the spent sorbents and fly ash was carried out. Methods employed include optical microscopy, scanning electron microscopy, energy dispersive analyses by X-ray, electron microprobe analysis, X-ray diffraction, emission and atomic absorption spectroscopy, and wet chemical methods. Tables 18 and 19 summarize the chemical composition of the spent sorbent and fly ash as determined by wet chemical methods. These are in agreement with the chemical species identified by X-ray diffraction that are listed in Table 20.

TABLE 18. CHEMICAL COMPOSITIONS OF SPENT BED MATERIALS AND FLY ASH FROM FLUIDIZED-BED COAL COMBUSTION UNITS

Sample	Process	Sorbent	Chemical Composition (w/o)				
			Ca	Mg	$SO_4^=$	$S^=$	$CO_3^=$
Argonne C2/C3 Spent Sorbent	Pressurized, once-through	dolomite	22.5	11.7	40.0	<0.05	5.1
Argonne VAR 4 Spent Sorbent	Pressurized, once-through	dolomite	20.6	12.0	27.5	0.04	8.7
Argonne REC-3 Spent Sorbent	Pressurized, regenerative (3rd cycle combustor)	dolomite	18.6	11.7	33.5	0.05	0.6
Argonne LST-1 Spent Sorbent	Pressurized, once-through	limestone	31.7	1.25	26.7	0.05	--
Argonne LST-2 Spent Sorbent	Pressurized, once-through	dolomite	20.0	13.4	31.4	0.04	--
Argonne LST-3 Spent Sorbent	Pressurized, once-through	dolomite	21.8	9.1	29.9	0.008	11.3
Argonne LST-4 Spent Sorbent	Pressurized, once-through	limestone	30.7	1.3	20.2	0.05	33.2
Argonne CCS-10 Spent Sorbent	Pressurized, regenerative (10th cycle regenerator)	dolomite	24.5	16.1	9.8	0.04	0.7
Exxon 8.4 Spent Sorbent	Pressurized, once-through	limestone	36.1	0.5	18.3	<0.05	34.8
Exxon 27 Spent Sorbent	Pressurized, once-through	Dolomite/ limestone	21.8	6.6	24.8	0.002	13.9
Exxon 30.2 Spent Sorbent	Pressurized, once-through	Limestone	33.4	1.5	17.3	0	30.0
Exxon 19.6 Spent Sorbent	Pressurized, once-through	Limestone	40.0	0.5	10.0	0.001	44.0
PER Spent Sorbent	Atmospheric, once-through	Limestone	19.1	0.9	20.1	0.04	0.6
Exxon 27 Fly Ash	Pressurized, once-through	Dolomite/ limestone	7.9	4.6	14.6	0	--
Exxon 19.6 Fly Ash	Pressurized, once-through	Limestone	7.4	0.8	7.1	0	--
Exxon 26 Fly Ash	Pressurized, once-through	Limestone	11.8	1.9	10.0	0.006	--
Exxon 34 Fines*	Pressurized, once-through	Dolomite	7.7	2.8	14.4	0	--

*Collected from flue gas sampling filter.

TABLE 19. CHEMICAL COMPOSITIONS OF SPENT SORBENTS FROM FLUIDIZED-BED COAL COMBUSTION

Sample	Process	Sorbent	Molar Fraction (Ca based)			
			$CaSO_4$	$CaCO_3$	CaO	CaS
Argonne C2/C3	Pressurized, once-through	Dolomite	0.71	0.15	0.14	<0.003
Argonne VAR 4	Pressurized, once-through	Dolomite	0.55	0.28	0.17	<0.003
Argonne REC-3	Pressurized, regenerative (3rd cycle combustor material)	Dolomite	0.75	0.02	0.23	<0.003
Argonne LST-1	Pressurized, once-through	Limestone	0.35	0.65	0	<0.003
Argonne LST-2	Pressurized, once-through	Dolomite	0.65	0.35	0	<0.003
Argonne LST-3	Pressurized, once-through	Dolomite	0.57	0.35	0.08	<0.003
Argonne LST-4	Pressurized, once-through	Limestone	0.27	0.72	0.01	<0.003
Argonne CCS-10	Pressurized, regenerative (10th cycle regenerator)	Dolomite	0.16	0.02	0.82	<0.003
Exxon 8.4	Pressurized, once-through	Limestone	0.21	0.64	0.15	<0.003
Exxon 27	Pressurized, once-through	Dolomite/ limestone	0.47	0.42	0.1	<0.003
Exxon 30.2	Pressurized, once-through	Limestone	0.22	0.60	0.18	<0.003
Exxon 19.6	Pressurized, once-through	Limestone	0.11	0.73	0.16	<0.003
PER	Atmospheric, once-through	Limestone	0.44	0.02	0.54	<0.003

Note that, in general, the spent sorbents consist of major amounts of sulfated and unsulfated limestone and a minor amount of silicon, whereas the fly ash contains mostly SiO_2, $CaSO_4$, and Fe_2O_3 but little unsulfated $CaCO_3$ or CaO. Exxon spent sorbent No. 27 was separated into dark and light particles. The light particles were found to contain sulfated and unsulfated dolomite ($CaCO_3$, $CaSO_4$, and MgO), but the dark particles were high in impurities consisting mostly of Fe_3O_4 spinel, with some SiO_2, $CaSO_4$, MgO, Fe_2O_3, and trace $CaCO_3$, CaS, and Al_2O_3.

TABLE 20. CHEMICAL COMPOSITION OF SPENT SORBENT AND FLY ASH BY X-RAY DIFFRACTION

Samples	Species Identified							
	$CaSO_4$	$CaCO_3$	CaO	MgO	SiO_2	αFe_2O_3	Fe_3O_4 Spinel	Others
Argonne C2/C3	Major	High minor	--	Major	--	--	--	
Exxon 8.4 Spent Sorbent	Major	Major	Major	--	--	--	--	CaS possible
Exxon 27 Spent Sorbent (dark particles)	High minor	Trace	--	Present	High minor	Minor	Major	CaS present Al_2O_3 present
Exxon 27 Spent Sorbent (light particles)	Major	Major	--	Major	Trace	--	--	--
Exxon 19.6 Spent Sorbent	Major	Major	--	--	Trace	--	--	--
Exxon 30.2 Spent Sorbent	Minor	Major	--	--	Trace	--	--	--
PER Spent Sorbent	Major	--	Minor	--	Minor	Trace	--	Ca SiO_3 possible
Exxon 27 Fly Ash	Major	--	--	--	Major	Major	--	--
Exxon 19.6 Fly Ash	Major	Trace	--	--	Major	High minor	--	--
Exxon 26 Fly Ash	Major	Minor	--	--	Major	High minor	--	--
Exxon 34 Fines	Major	--	--	Present	Major	High minor	--	Ca SiO_3 possible

Table 21 compares the compositions of the actual spent sorbents with their projected values (Section 4). The most significant difference exists in the case of the pressurized, once-through system where the unsulfated sorbent exists as a mixture of $CaCO_3$ and CaO instead of CaO alone, as projected.

Spent sorbents from the fluidized-bed combustion process are often inhomogeneous. Figure 11 shows photomicrographs of the spent sorbents and fly ash from Exxon run No. 27, showing variations in particle size, color, shape, and texture.

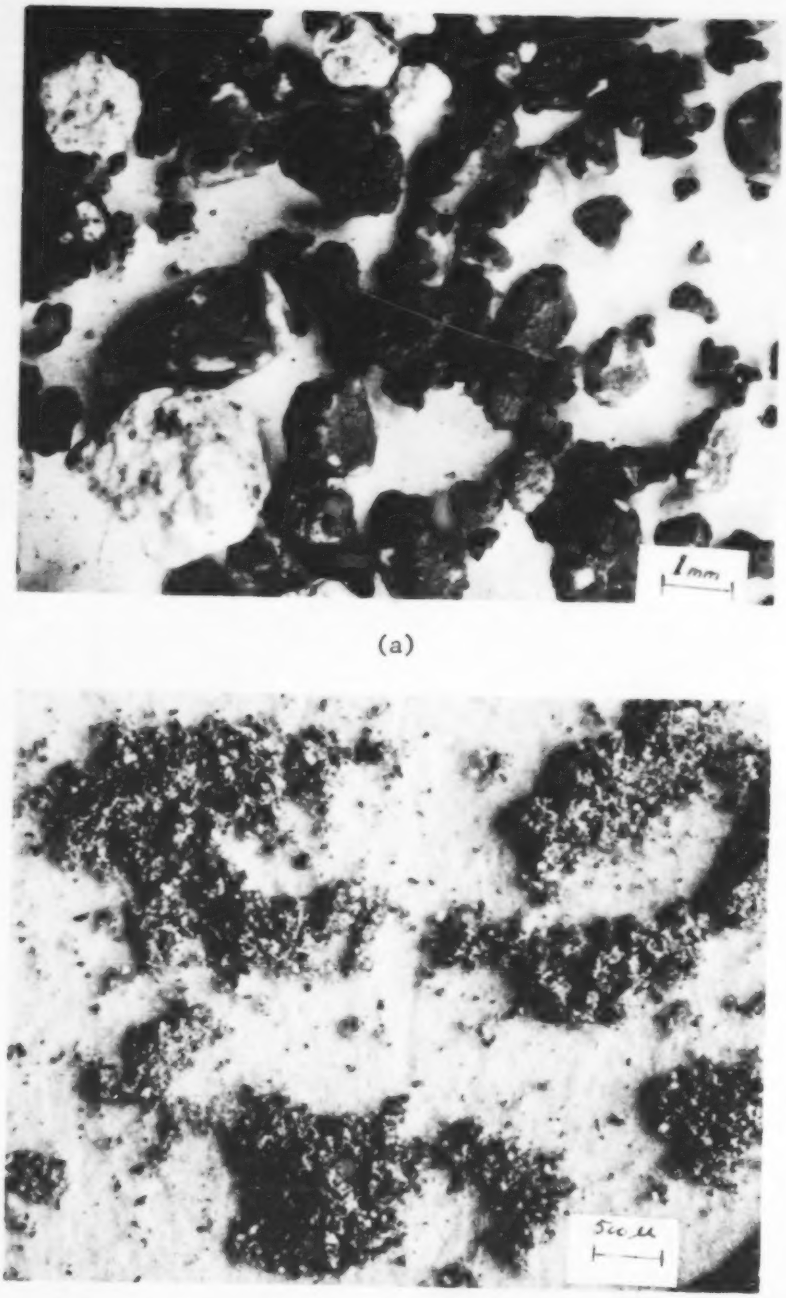
Trace metal element distribution was investigated by scanning electron microscopy (SEM) in conjunction with energy dispersive analysis by X-ray (EDAX). Figure 12 shows a typical SEM photomicrograph of a spent sorbent (Exxon No. 27). The EDAX spectra, which plot peak intensity versus X-ray energy, are shown on Figures 4(b) and (c) for two locations on the spent sorbent particle as marked on Figure 12(a). The presence of calcium, silicon, aluminum, sulfur, iron, sodium, potassium, and titanium is indicated. A similar SEM photomicrograph and EDAX plots are shown for a fly ash sample (Exxon 19.6) in Figure 13. Much higher silicon and aluminum and lower calcium peaks are observed for the fly ash sample.

Electron microprobe analysis provided the elemental profiles of partially sulfated limestone or dolomite particles when polished cross sections were scanned. One persistent phenomenon was that the partially sulfated limestone or dolomite always displayed a high concentration of sulfur at the periphery of the particle and that the sulfur extended into the particle along the grain boundaries or cracks. Figure 14 shows photomicrographs of area scans for sulfur at two locations (edge and center) on the cross section of a partially sulfated limestone particle illustrating this effect. The sulfur concentration is proportional to the intensity of the white dots on the area scan photos. Another finding revealed by the electron microprobe was that the highly sulfated periphery was not only rich in sulfur but also high in silicon, aluminum, and iron. The high concentrations of silicon, aluminum, and iron at the surface

TABLE 21. COMPARISON OF CHEMICAL COMPOSITIONS OF ACTUAL SPENT SORBENTS FROM FLUIDIZED-BED COMBUSTION UNITS WITH THE PROJECTED VALUES

Process Conditions	Actual Spent Sorbent (Molar Fraction Ca-Based)				Projected Composition (Molar Fraction Ca-Based)			
	$CaSO_4$	CaO	$CaCO_3$	CaS	$CaSO_4$	CaO	$CaCO_3$	CaS
Atmospheric Pressure,* Limestone Sorbent, Once-through	0.44	0.54	0.02	<0.003	0.25	0.75	0	0
Pressurized, Limestone Sorbent, Once-through	0.11-0.35	0-0.18	0.60-0.73	<0.003	0.40	0.60	0	0
Pressurized, Dolomite Sorbent, Once-through	0.47-0.71	0-0.23	0.15-0.42	<0.003	0.80	0.20	0	0
Pressurized, Dolomite Sorbent, Regenerative	0.16	0.82	0.02	<0.003	0.34	0.61	0	0.05

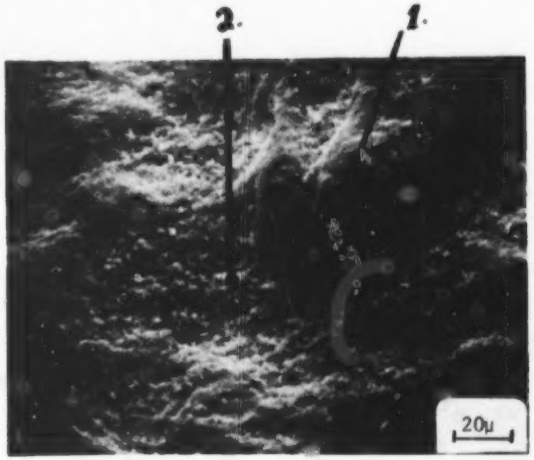
*The only sample available is an unidentified PER sorbent with unknown history and a typical sulfation level.



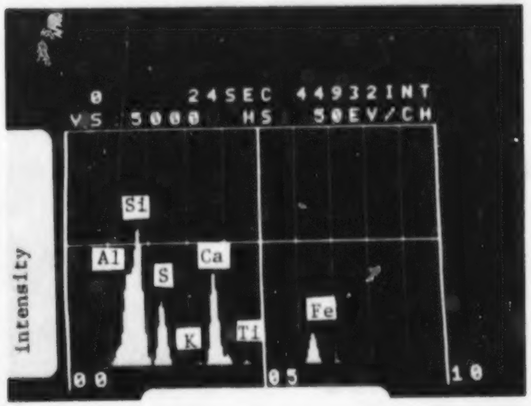
(a)

(b)

Figure 11. Microphotographs of Exxon Run No. 27 (a) Bed Stone and (b) Fly Ash.

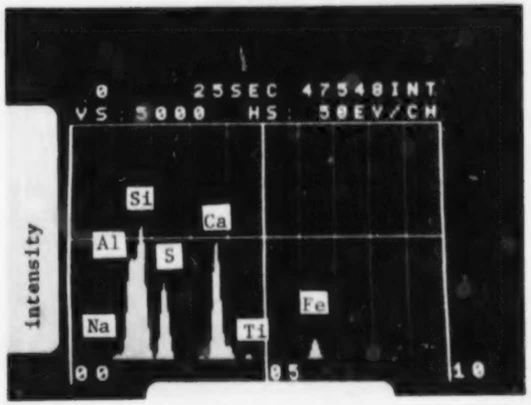


(a)



energy, KeV

(b)



energy, KeV

(c)

Figure 12. (a) SEM Photomicrograph of Exxon 27 Spent Sorbent
(b) EDAX Spectrum of Spot 1 on SEM
(c) EDAX Spectrum of Spot 2 on SEM

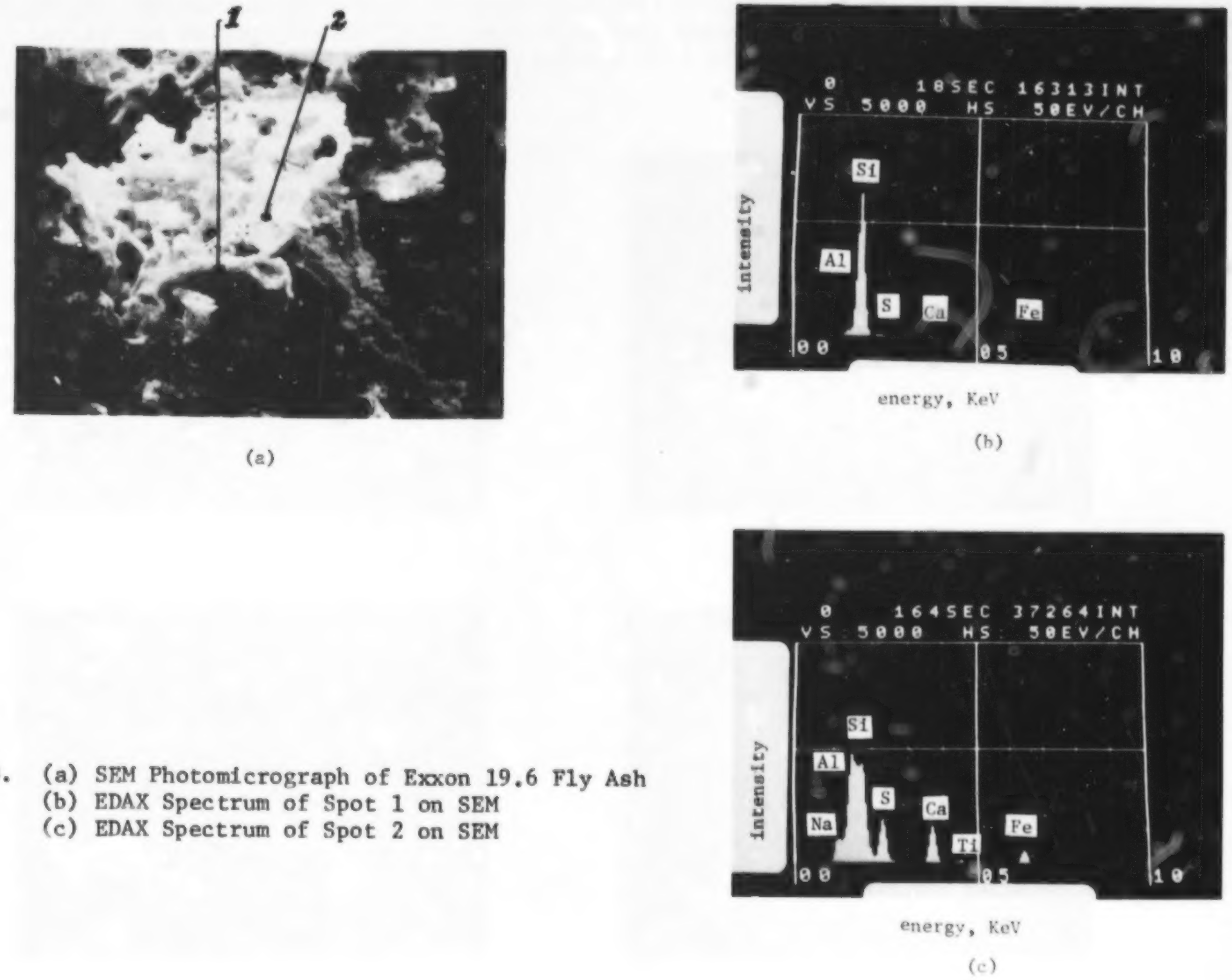


Figure 13. (a) SEM Photomicrograph of Exxon 19.6 Fly Ash
(b) EDAX Spectrum of Spot 1 on SEM
(c) EDAX Spectrum of Spot 2 on SEM

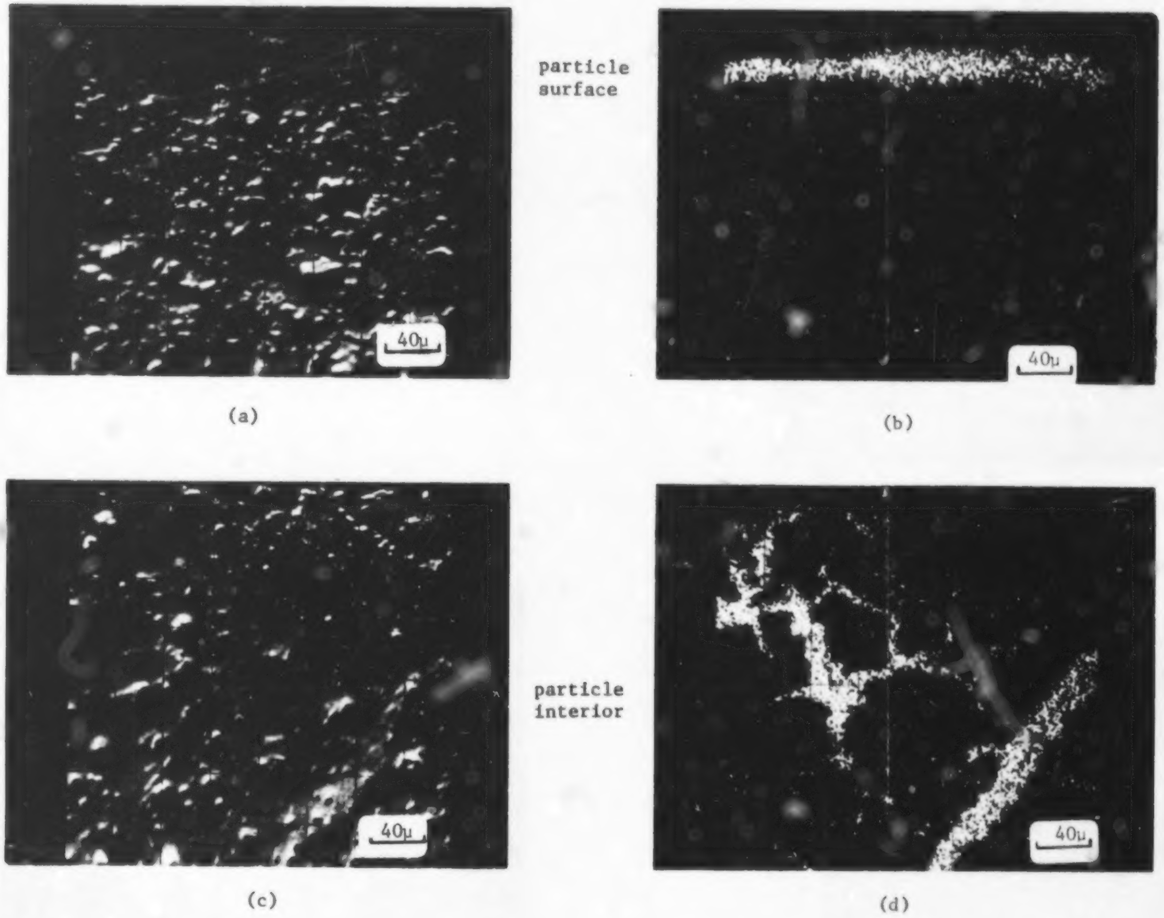

particle
surface
particle
interior
40µ
40µ
40µ
40µ
(a)
(b)
(c)
(d)

Figure 14. SEM and Electron Microprobe Photomicrographs of a Spent Limestone Particle (Exxon 27)
(a)(b) SEM and Sulfur Scan on a Cross-Sectional Area Near the Surface
(c)(d) SEM and Sulfur Scan on a Cross-Sectional Area in the Interior.

were also observed for particles that were totally sulfated. TVA recently reported that a 2 to 5μm thick hematite deposition was found on the sorbent particles.(35) Figures 15 and 16 show the photomicrographs of electron microprobe analysis for a partially and a completely sulfated limestone particle. The surface coating is suspected to have significant influence on the reaction mechanism and leaching behavior, but the implication is not yet fully understood.

Trace metal ion concentrations on spent sorbent and fly ash were determined by emission and atomic absorption spectroscopy. Results are summarized in a later section, together with trace elements found in their leachates.

Leaching Tests

At this time, there is no standard EPA leaching test with which the potential environmental contamination from a solid waste can be assessed. Currently, EPA's Office of Solid Waste, Hazardous Waste Management Division is developing a "standard" leach test method as part of its effort in the development of national standards for hazardous waste definition to be promulgated under RCRA Section 3001, planned for April, 1978. Parallel to the EPA effort, ASTM committee 19.12 (subcommittee 19.1203) is also developing standard leaching tests for solid waste in general. A shake test is proposed by both efforts.

In this study leachates are induced by shake tests, except where otherwise specified. Samples of waste stones were mixed with deionized water in Erlenmeyer flasks at room temperature. An automatic shaker capable of 70 excursions per minute was used to agitate the mixtures. Among the parameters investigated were sorbent/ water loading, sample mixing time, and aerobic versus anaerobic leaching conditions, with the latter shake under nitrogen atmosphere. The supernatants resulting from this operation were filtered, and the filtrate was determined for pH, specific conductance, calcium, magnesium, sulfide, sulfate trace metal ion concentration, and total organic carbon content. The solid samples before and after the leaching operation were also analyzed for their chemical and physical characteristics.

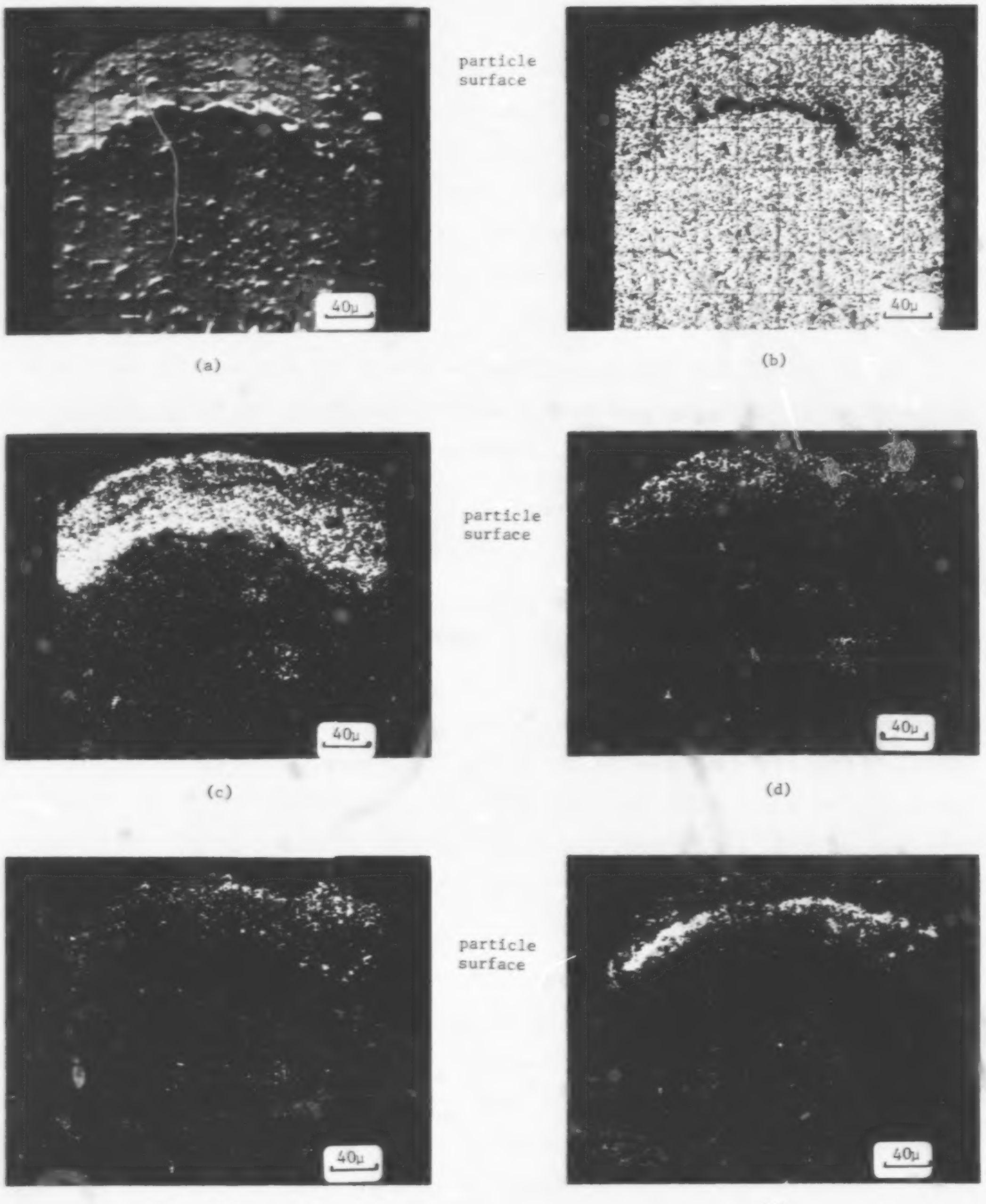
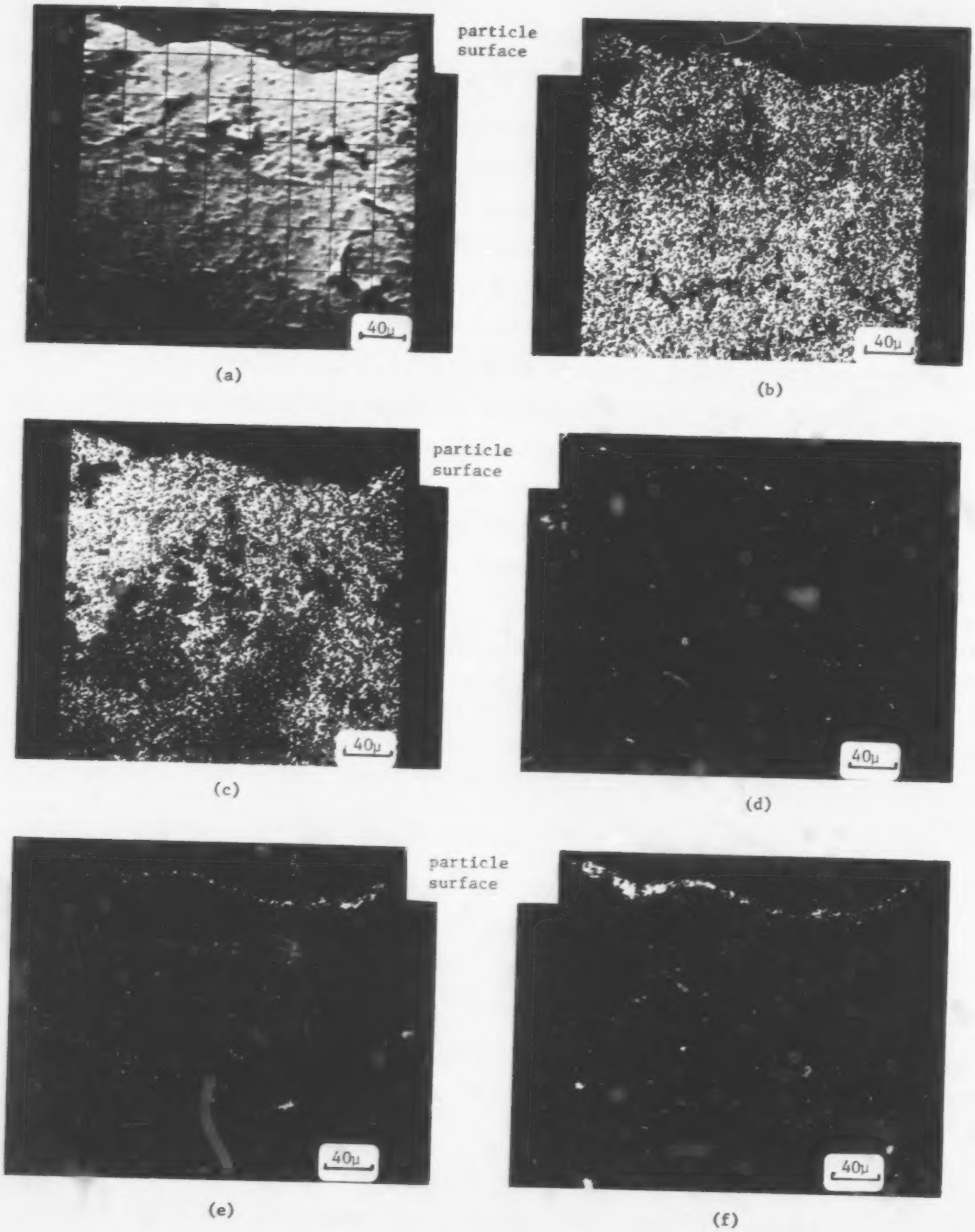

particle
surface
40μ
(a)
(b)
(c)
(d)
(e)
(f)

Figure 15. Area-Scan Electron Microprobe Photomicrographs on a Cross Section of a Spent Limestone Particle (Exxon 19.6) Near Its Surface, (a) SEM, (b) Ca, (c) S, (d) Si, (e) Al, and (f) Fe


particle
surface
40µ
40µ
particle
surface
40µ
40µ
particle
surface
40µ
40µ

(a) (b) (c) (d) (e) (f)

Figure 16. Area-Scan Electron Microprobe Photomicrographs on a Cross Section of a Completely Sulfated Spent Limestone Particle (Exxon 19.6) Near Its Surface, (a) SEM, (b) Ca, (c) S, (d) Si, (e) Al and (f) Fe.

Two shake procedures have been employed. These are described below.

- Continuous shake test. It establishes equilibrium conditions between the solid and its aqueous surrounding and provides the worst possible case with respect to contamination release. This method has been used by Westinghouse since 1975 as one of the screening tests for determining leaching properties of FBC spent solids. Typically a 1:10 solid-to-water ratio is used.
- Intermittent shake test. A series of ten to fifteen cycles of a 72-hour shake test was adopted as part of the leachability study to provide leaching rate, aging effect, and long-term leachability of the worst case and to make possible the calculation of "total fraction leached" for any specific ion or for TDS as a function of total leach time or total leachate passing the sample. Leachates are analyzed at the end of each interval and a fresh charge of deionized water is added for each 72-hour leach cycle. Typically, a 1:3 solid-to-water ratio is used.

Both shake tests are more severe than conditions anticipated under actual land disposal; results from the shake tests are expected to project the worst.

Spent Sorbent

Leaching properties were investigated for 13 batches of actual spent bed materials (limestone and dolomite) from a pilot-scale fluidized-bed combustor and regenerator operated under atmospheric and elevated pressures. The operating conditions and chemical compositions of these sorbents, which underwent standard shake tests, are presented in Tables 18 and 19.

Since calcium sulfate is a major constituent of the waste stone from the fluidized-bed combustion process and leachates contained high calcium and sulfate concentrations, a naturally occurring gypsum was tested under similar leaching conditions for comparison.

Figure 17 presents the chemical characteristics of leachates as a function of continuous leaching time and compares them with gypsum leachate. It shows that leachates of the Exxon spent sorbents (all limestone except Exxon No. 27, which was a mixture of limestone and Pfizer dolomite) displayed similarly high calcium, sulfate, alkalinity, and total dissolved solids, independent of operating conditions. Leachates of Argonne's once-through spent dolomite exhibited noticeably lower TDS and calcium, approximately in the range of gypsum leachate. Negligible magnesium ion concentration was found in leachates of spent dolomite sorbent (<20 ppm). It appears that dolomite sorbent, when generated under similar fluidized-bed conditions, produces leachate of better quality. Spent dolomite from either the combustor or the regenerator of the regenerative mode, however, produced leachate worse than the once-through spent dolomite sorbent. Further testing employing the 15 x 72 hour intermittent shake method indicated that the leachate quality of Exxon 19.6 spent limestone improved much faster than did leachate from Argonne C2/C3 spent dolomite, although the initial leachate for the spent dolomite was much better.

Leachates or PER spent limestone from the atmospheric fluidized-bed unit displayed similar chemical properties as did those of Exxon spent limestones which were generated under elevated pressure. Since the PER sorbent was the only atmospheric sample tested and it was not representative due to an unidentified origin, operating conditions, and storage age, the leaching behavior of spent sorbent generated under atmospheric pressure should be investigated further.

Specific conductance has been shown to be a good index for leachate quality, since it represents the total dissolved solids in the system. Table 22, which compares the specific conductance of various sorbent systems, shows clearly the results observed in Figure 17 as described above.

Figure 18 shows leachate characteristics as a function of stone loading. Again, it shows that the leachate from Argonne's spent dolomite was of better quality than that of Exxon's spent limestone.

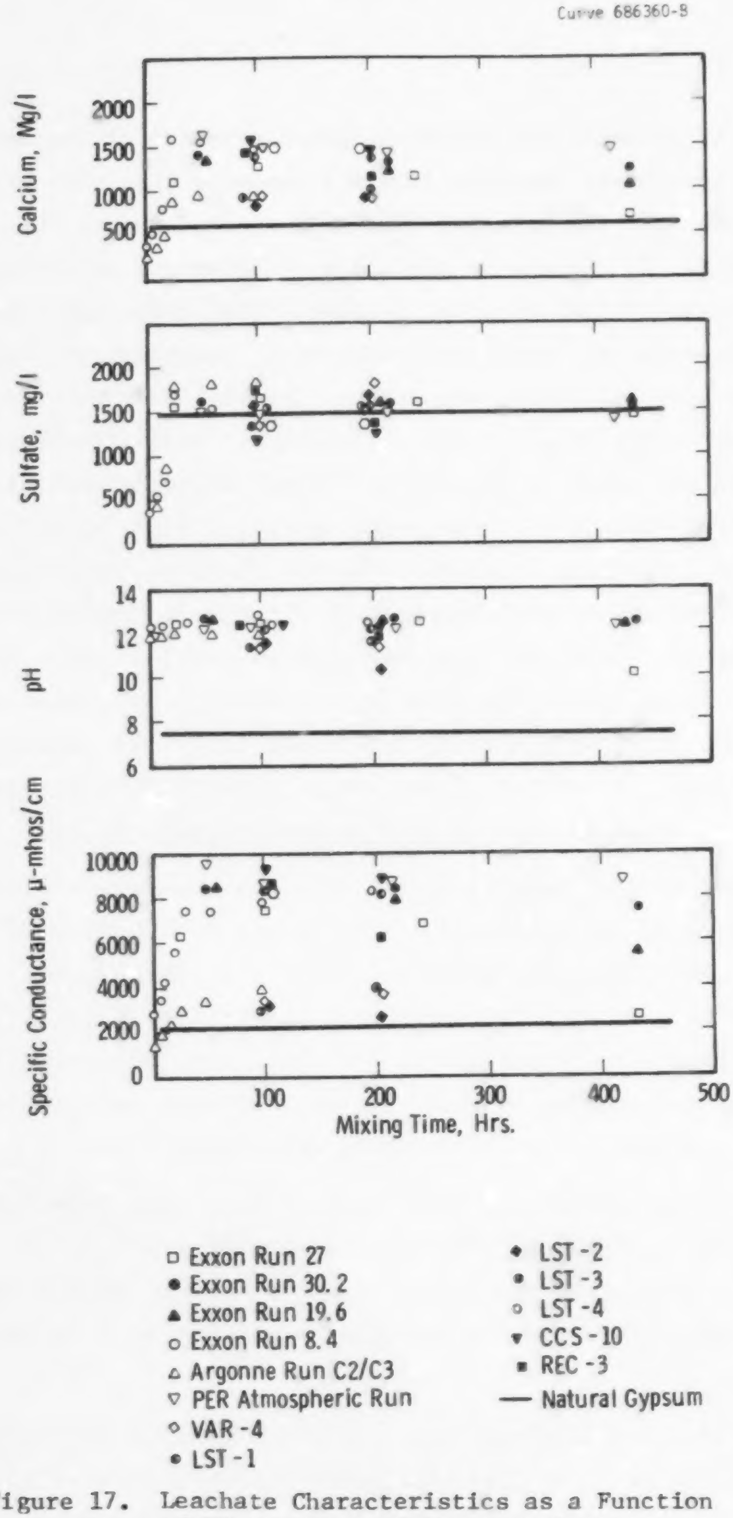


Figure 17. Leachate Characteristics as a Function of Mixing Time of Spent Sorbents

TABLE 22. COMPARISON OF SPECIFIC CONDUCTANCE OF LEACHATES FROM SPENT BED MATERIALS FROM VARYING FBC PROCESSES

Sample Identification	Process Variation	Specific Conductance (μ-mhos/cm)
Argonne C2/C3	Dolomite, once-through, pressurized system	3980
Argonne VAR-4	Dolomite, once-through, pressurized system	3510
Argonne LST-2	Dolomite, once-through, pressurized system	3310
Argonne LST-3	Dolomite, once-through, pressurized system	3140
Argonne REC-3	Dolomite, regenerative, pressurized system	8710
Argonne CCS-10	Dolomite, regenerative, pressurized system	9540
Argonne LST-1	Limestone, once-through, pressurized system	8540
Argonne LST-4	Limestone, once-through, pressurized system	8570
Exxon 8.4	Limestone, once-through, pressurized system	7760
Exxon 30.2	Limestone, once-through, pressurized system	8000-8500
Exxon 19.6	Limestone, once-through, pressurized system	8000-8500
PER	Limestone, once-through, atmospheric system	8590

In addition to the shake test, a small column leaching experiment was conducted on Argonne's spent dolomite and gypsum at a constant run-off rate. Solid residues were manually packed into the columns of 11 mm dia. to 213 mm depth. Successful 250 ml leachates were collected at a flow rate of 5 ml/min. Results plotted in Figure 19 showed equilibrated calcium and sulfate concentrations but a gradual decrease in total dissolved solids and leachate alkalinity. It showed that the leachate characteristics of Argonne's spent dolomite were comparable to or better than the gypsum leachate except for Argonne's higher pH.

Sulfide was not found in spent bed sorbent or its leachate for the once-through system. Some sulfide (∿25 ppm) was found in the anaerobic leachate from the regenerated sorbent. This may not be a problem because

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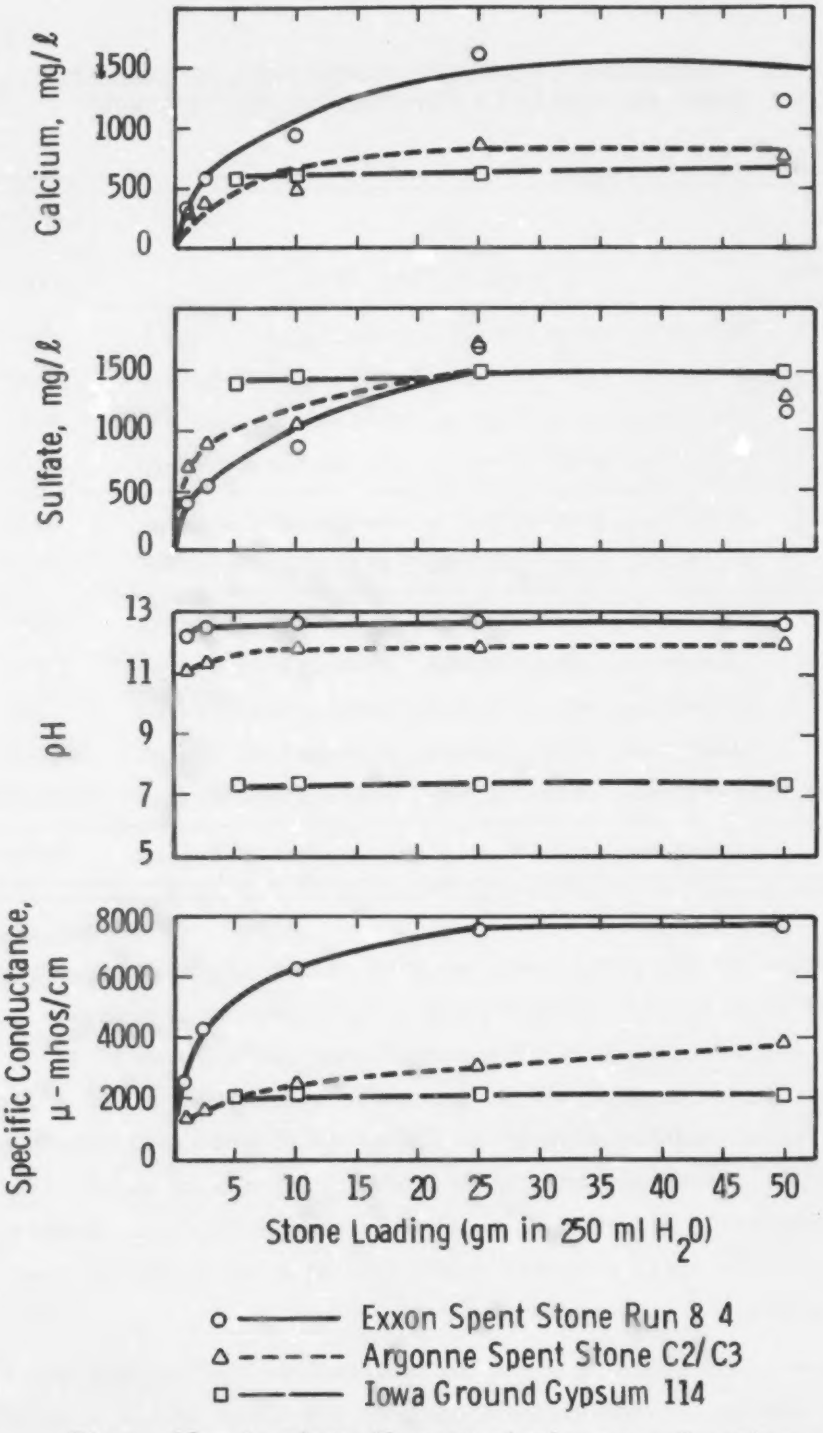

Figure 18. Leachate Characteristics as a Function of Stone Loading

Curve 686469-A

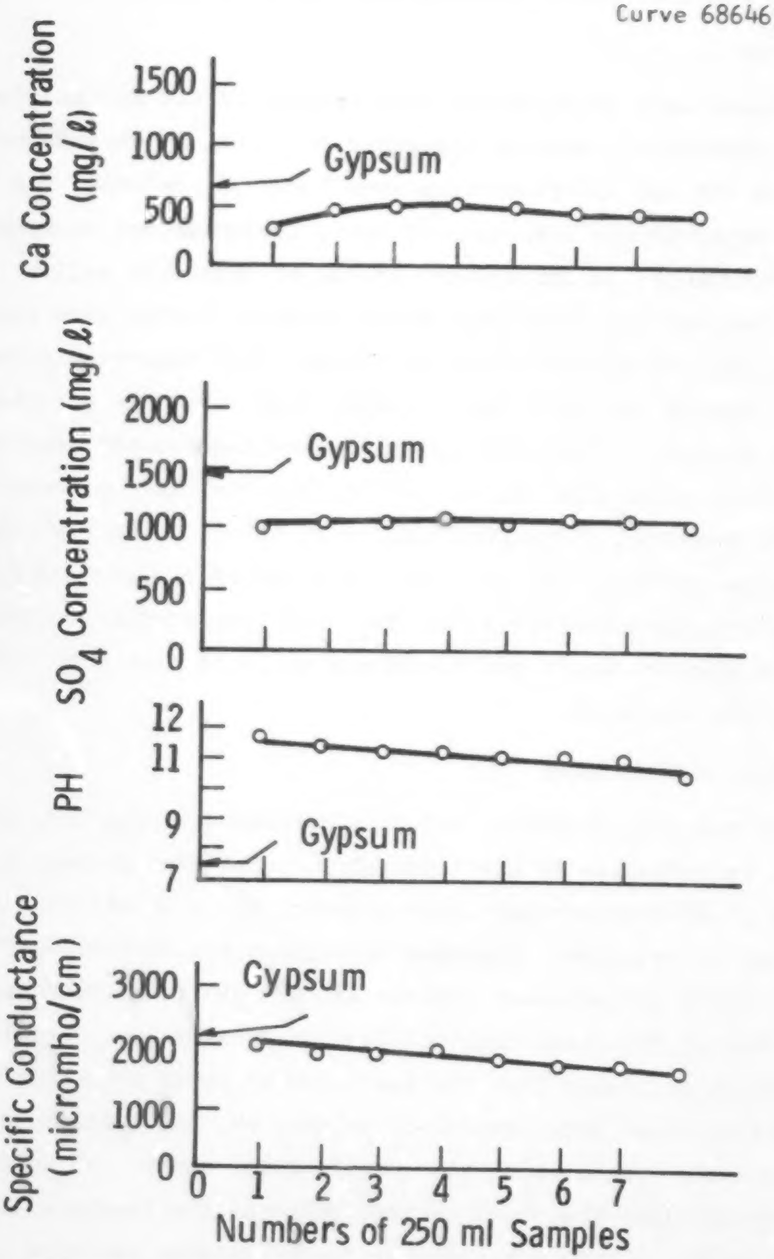

Figure 19. Leachate Characteristics of the Argonne Spent Stone C2/C3 Leachates Induced by the Column Tests

of the apparent ease of air oxidation of sulfide under aerobic conditions. Since only limited quantities of regenerative sorbent were available for testing at this time, further investigation should be conducted in the future.

Fly Ash and Fines

Leaching tests were conducted on four batches of fly ash and fines from the Exxon miniplant. Results presented in Figure 20 showed that the leachates of fly ash and fines displayed lower pH, calcium, and TDS than did those found in the leachates of spent limestone bed materials. This could be attributed to the greater amount of insoluble silica present in fly ash and the relatively small amounts of free lime that might be either partially dead-burned or covered with impermeable $CaSO_4$ because of its smaller particle size or might form insoluble pozzolanic reaction products (e.g., aluminosilicates) during the aqueous leaching process. The fines (Exxon No. 34) collected from the flue gas sampling system produced leachates of quality similar to those of the fly ash collected from the cyclone. In general, leachates of fly ash and fines displayed chemical characteristics (Ca, $SO_4^=$, and TDS) similar to those of the gypsum leachates except for the higher pH of fly ash. No sulfide was present in the leachates.

Spent Sorbent/Fly Ash Mixtures

Since both the spent sorbent, which is generated in the bed, and the fly ash, which is collected in the particulate collection device, are produced from the fluidized-bed combustion process, it is likely that they will be disposed of together. Mixtures of various ratios (80/20, 70/30, 50/50, 30/70, 20/80) of the spent sorbent and fly ash from Exxon runs 27 and 19.6 were tested for their combined leaching properties. Results shown in Figure 21 indicated that the leachates of spent sorbent/fly ash mixtures displayed lower total dissolved solids, pH, and calcium concentration than did the leachates of the spent sorbent alone. An addition of >20 wt % fly ash into the spent sorbent improved the leachate characteristics noticeably, possibly because of the pozzolanic reaction between the free CaO present in the spent sorbent and the SiO_2 and Al_2O_3 present in the fly ash to form insoluble compounds.

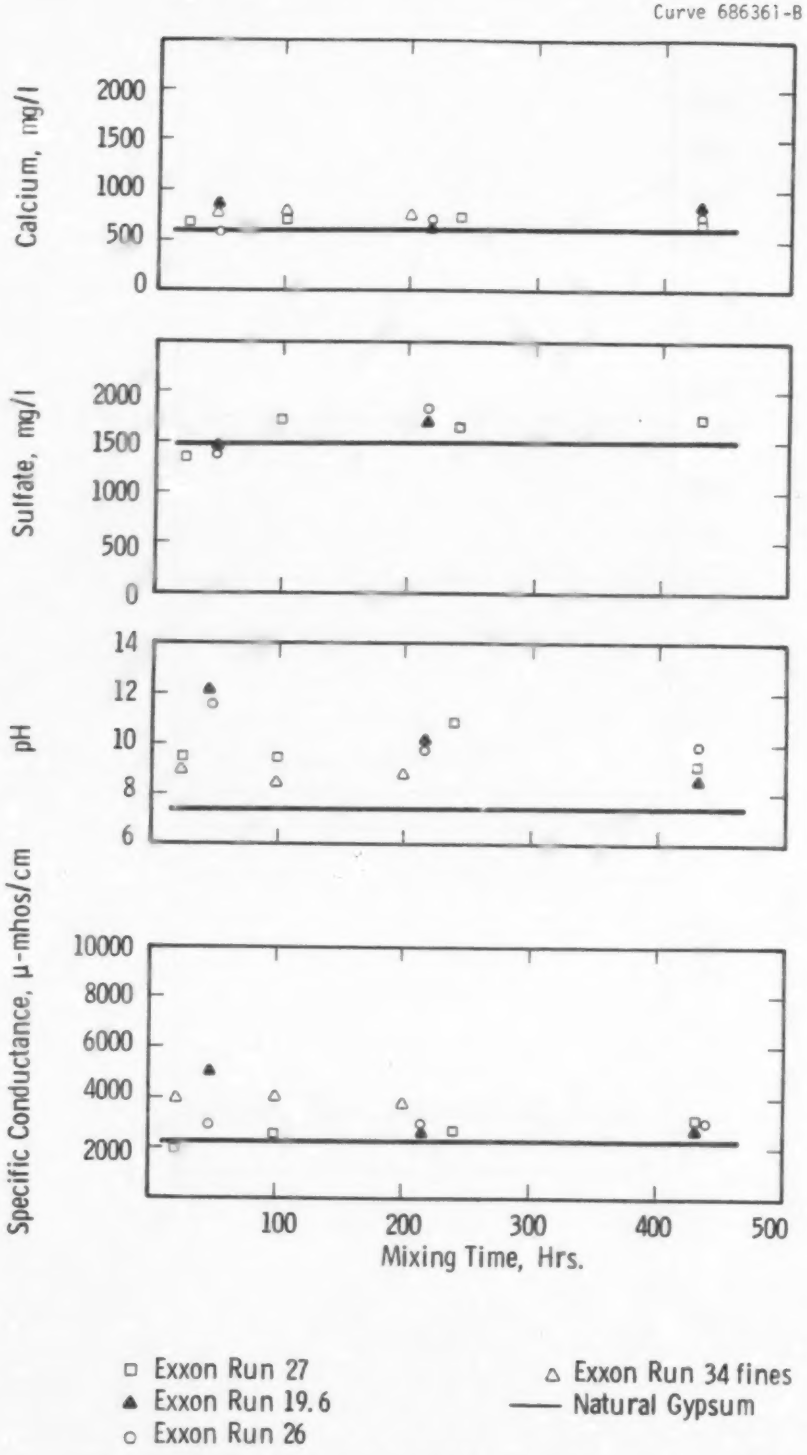

Figure 20. Leachate Characteristics as a Function of Mixing Time of Fly Ash

Curve 686359-B

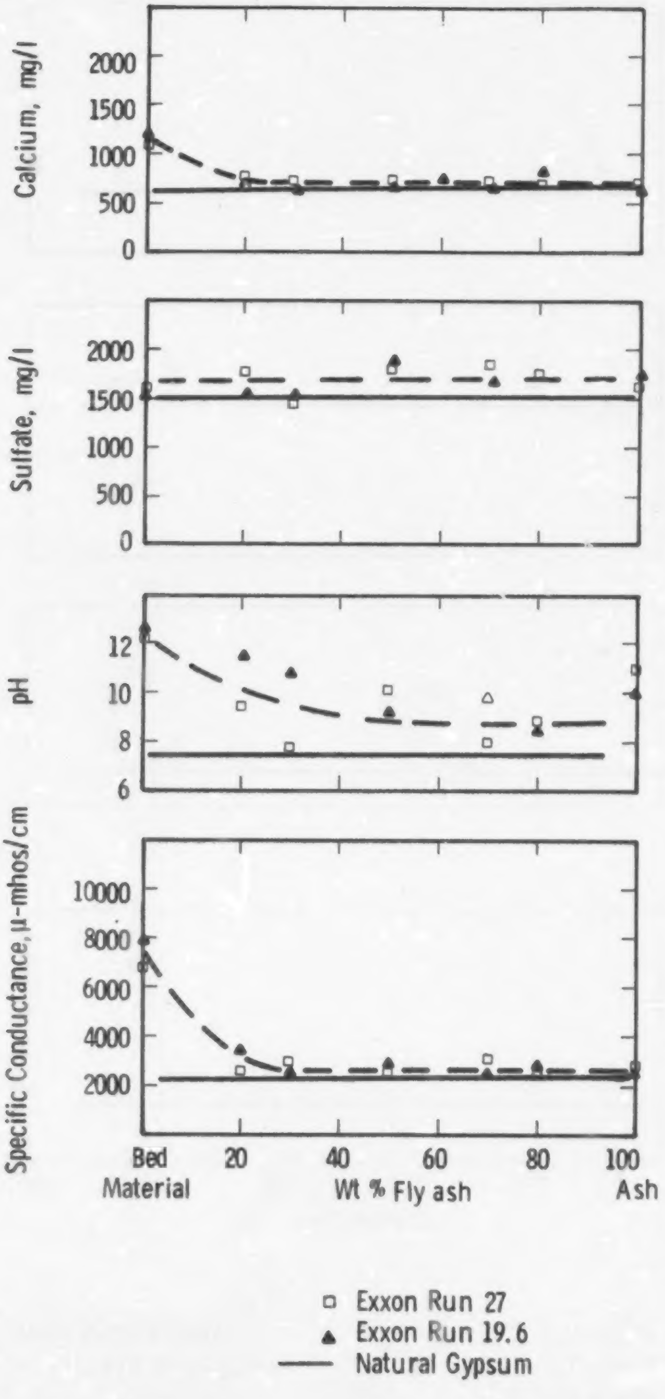

Figure 21. Leachate Characteristics of Bed Material/Fly Ash Mixtures

Processed Spent Sorbent/Fly Ash Compacts

Leaching property was investigated for the processed cubes prepared by room temperature compacting of sorbent/ash blends, (see identification of the blends on p. 52). Among the parameters investigated are the sorbent/ash mixing ratio and the air curing time. These cubes, prepared in duplicate, were leached by two procedures. One of the cubes was leached by the continuous shake for 1000 hr. The other underwent the 15 x 72 hr intermittent shake cycles. Figure 22 compares the leaching rates of four processed sorbent/ash compacts with different mixtures and air curing time. Several preliminary observations can be made from the up-to-date data presented in Figure 22.

(1) The leachate quality improves with time. The amounts of solid leached (e.g., TDS, Ca, SO_4) decrease significantly with the total number of 72-hour consecutive leach periods. The decreasing leach rate with time is most likely attributable to the formation of the practically insoluble $CaCO_3$ on the sample surface and within the pores, which would retard the solid dissolution. Indeed, a white $CaCO_3$ scale was observed on the surface of these cubes and on the container wall after leaching.

(2) The leachate pH also decreases gradually with time. This is also attributed to the neutralization effect of CO_2 from the air.

(3) Leachates from cubes made from mix II (10 wt % fly ash) had a lower initial SO_4 concentration and a higher initial pH than did those of mix I (36 wt % fly ash) cubes, but they fell within the same range after approximately 400 hours of leaching. It should be pointed out that the compacts made from 10 wt % fly ash also had higher compressive strength.

(4) The leaching properties were relatively independent of the air curing time of the compacts within the experimental range.

Table 23 compares the chemical characteristics of leachates from the unprocessed Exxon run 27 spent bed material, fly ash, and their mixtures with those of the processed Exxon run 27 sorbent/ash blends. Note that

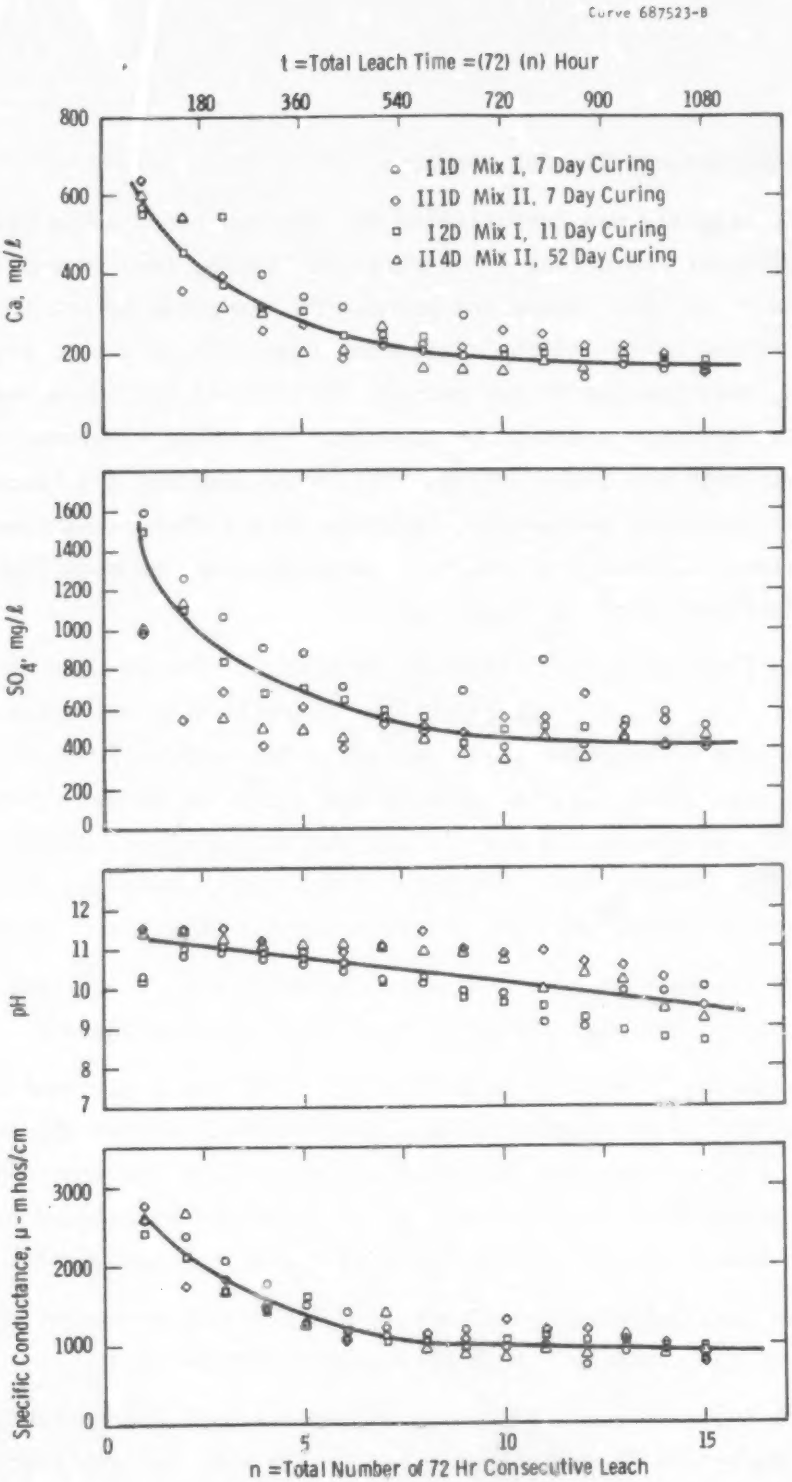

Figure 22. Chemical Characteristics from Consecutive Leachates for Processed Exxon No. 27 Spent Sorbent/Fly Ash Compacts

TABLE 23. LEACHATE CHARACTERISTICS OF PROCESSED AND UNPROCESSED SPENT SORBENT AND FLY ASH FROM EXXON RUN 27

Sample		Leaching Condition	Leachate Characteristics			
			pH	Specific Conductance (μ-mhos-cm^{-1})	Ca (Mg/ℓ)	SO$_4$ (Mg/ℓ)
Unprocessed	Exxon 27 spent sorbent	10 g/100 ml/100 hr Cont.	12.4	6320	1128	1512
	Exxon 27 fly ash	10 g/100 ml/100 hr Cont.	9.5	2490	684	1711
	Exxon 27 sorbent/ash mixture (80:20)	10 g/100 ml/197 hr Cont.	9.5	2570	760	1783
Processed Compacts	I1C: 36 wt % fly ash, 7 day cure	174 g/1740 ml/1224 hr Cont.	8.5	2550	576	1692
	I1D: 36 wt % fly ash, 7 day cure	182 g/546 ml/72 hr 1st 72 hr cycle	10.3	2580	572	1600
	I2C: 36 wt % fly ash, 11 day cure	181.5 g/1815 ml/1080 hr	7.7	2570	552	1410
	I2D: 36 w/o fly ash, 11 day cure	180 g/540 ml/72 hr	10.2	2430	552	1493
	12D: 36 wt % fly ash, 11 day cure	180 g/540 ml/[illegible] hr	10.2	2430	552	1493
	II1C: 10 wt % fly ash, 7 day cure	220 g/2200 ml/1224 hr	8.4	2230	560	1366
	II1D: 10 wt % fly ash, 7 day cure	220 g/660 ml/72 hr	11.5	2740	640	983
	II4C: 10 wt % fly ash, 52 day cure	216.5 g/2165 ml/1080 hr	8.3	2370	544	1548
	II4D: 10 wt % fly ash, 52 day cure	220 g/660 ml/72 hr	11.4	2590	600	1083

the processed sorbent/ash compacts generated leachates of quality superior to the unprocessed spent sorbent alone. This improved leaching property was also observed in leachates from mixtures of unprocessed sorbent and ash mixtures, as reported in the previous section.

Specific conductance is a measurement of total dissolved solids in a solution and serves as a good index for leachate quality. Figure 23 shows a log-log plot of specific conductance versus total leach time and total leachate volume passing through the solid for the sorbent/ash compact, compact crushed to powder, unprocessed sorbent/ash mixtures, and gypsum; and shows a straight line relation. The data in Figure 23 can be extrapolated to long-term leachability to indicate that gypsum leached constantly, independently of the total leach time and the volume of leachate passing the sample. On the other hand, the leachates from the sorbent/ash compact, the crushed compact powder, and the unprocessed sorbent/ash mixture displayed improvement with time and total volume and, therefore, are much less contaminating than are the natural gypsum from their long-term leachability. Finally, these results clearly demonstrate that the sorbent/ash compacting process improves the leaching property and reduces the potential environmental impact through leachate contamination.

Trace Metal Elements

Leachability of trace metal elements was determined by emission and atomic absorption methods. Table 24 summarizes the heavy metal concentrations in the spent sorbent and fly ash from the fluidized-bed coal combustion process and their leachates based on data from all the available residues. The National Primary Drinking Water Standards(16) and Public Health Service Regulations(17) and World Health Organization(18) as well as the EPA guidelines and standards for power plant effluent(8) are listed for comparison. It should be noted that the leachability of the trace metal ions was so low for all the spent sorbent

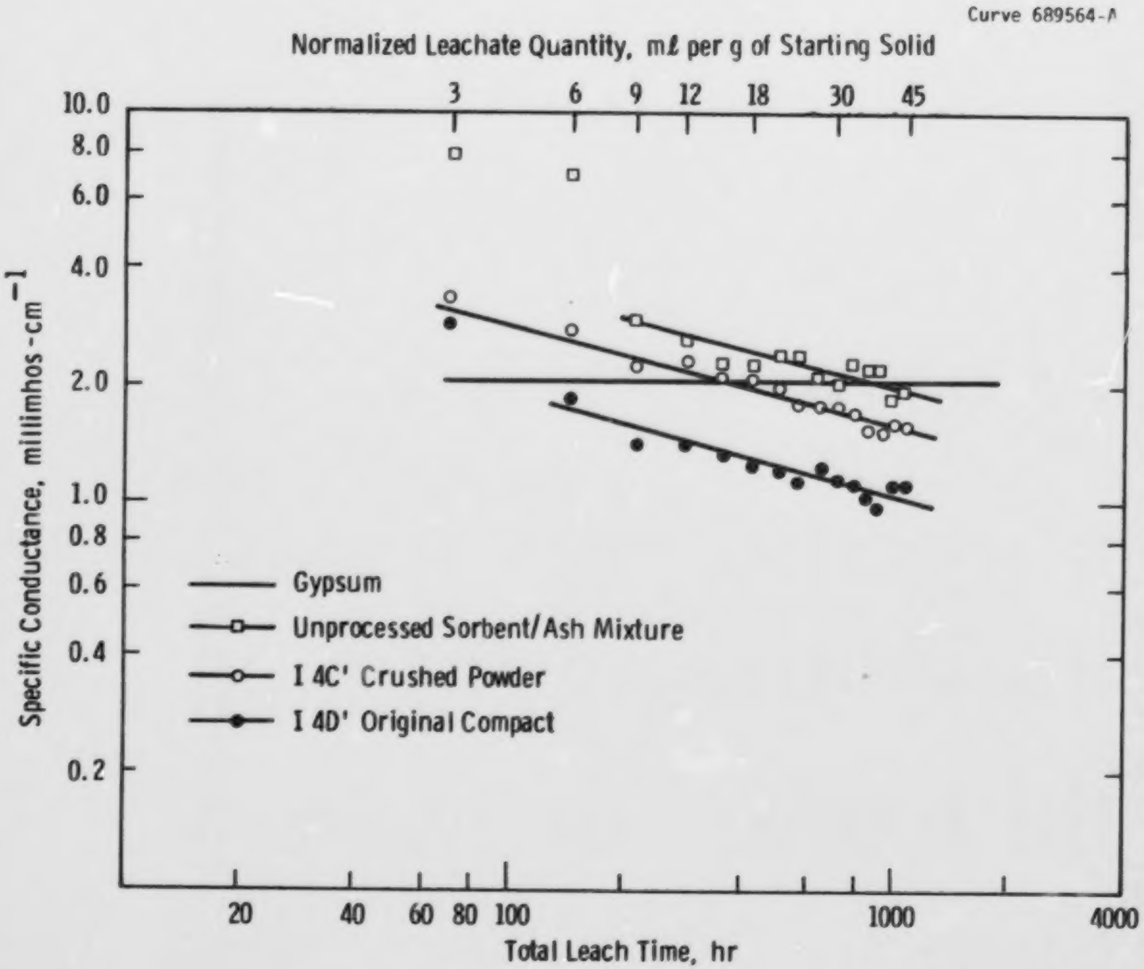

Figure 23. Comparison Specific Conductance of Leachate from Sorbent Compact, Crushed Compact, Unprocessed Mixture, and Gypsum

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TABLE 24. TRACE METAL ION CONCENTRATIONS IN SPENT SORBENTS AND FLY ASH FROM THE FLUIDIZED BED COMBUSTION PROCESS AND LEACHATES

Substance	Solid wt %		Leachates (mg/l)		National Primary Drinking Water Standards (mg/l)	Proposed Guidelines for Power Plant Effluent (mg/l)
	Bed Material	Fly Ash	Bed Material	Fly Ash		
Ag	<0.001	<0.001	<0.01	<0.01	0.05	
Al	0 to 5	0 to >10	<0.1	<1.0		
As	<0.03	<0.05	<0.05	<0.05	0.05	
B	<0.03	0.01 to 0.1	<0	<5.0		
Ba	<0.02	--	--	--	1.0	
Be	<0.0005	<0.003	<0.02	<0.02	1.0	
Bi	<0.01	<0.01	<0.04	<0.04		
Ca	>10	>1	>500	>500		
Cd	<0.006	<0.03	<0.04	<0.04	0.01	
Co	<0.01	<0.01	<0.1	<0.1		
Cr	<0.02	<0.1	<0.04	<0.04	0.05	0.2
Cu	<0.02	<0.02	<0.04	<0.1	1.0	1.0
Ge	--	<0.01	<0.1	<0.1		
Fe	2 to 5	0 to >10	<0.04	<0.04	0.3	1.0
Hg	ND <0.02	--	<0.001	<0.001	0.002	
K	0.2	--	<0.5	--		
Li	<0.01	--	<0.2	--		
Mg	0 to >10	<0.1	<30	0 to <300*		
Mn	<0.05	<0.05	<0.04	<0.04	0.05	
Mo	0.1	<0.01	<0.1	<1.0		
Na	<0.01	--	>10	--		
Ni	<0.01	<0.1	<0.04	<0.1	2.0	
Pb	<0.01	<0.05	<0.04	<0.4	0.5	
Sb	<0.01	<0.05	<0.08	<0.08		
Se	ND**	ND	<0.005	<0.005	0.01	
Si	0.1 to >10	>10	<2.0	0 to 30		
Sn	<0.005	<0.01	<0.04	<0.04	1.0	
Ti	0.01 to >1	0.1 to <10	<0.04	<0.04		
V	<0.05	<0.05	<0.1	<0.1		
Zn	<0.03	<0.1	<0.4	<0.4	5.0	1.0
Zr	<0.02	<0.1	<0.05	<0.05		

*High value resulted from leachate of fines collected from the flue gas particulate collection

**ND - Not detected.

and fly ash that none of the leachates exceeded the drinking water standards. Leachates from the processed sorbent/ash compacts displayed similarly low trace element concentrations. Although the levels of detection were in some cases limited by the analytical sensitivity achieved with the small quantity of samples available, the leachability of trace metal ions from the spent sorbents and fly ash from the fluidized-bed combustion process will probably not cause water pollution problems, at least for those trace metals covered by some form of drinking water standard. This is easily understood since the leachates from a spent limestone or dolomite system are highly alkaline and suppress the heavy metal dissolution, since their solubility in an alkaline environment is governed by their practically insoluble hydroxides and carbonates.

COD/BOD/TOC

Determination of chemical oxygen demand (COD) provides a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. The dichromate reflux method is usually employed for the COD determination because it has advantages over other oxidants in oxidizability. The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of waste waters, effluents, and polluted waters. The test is of limited value in measuring the actual oxygen demands of surface waters; and the extrapolation of test results to actual situations is highly questionable, since the laboratory environment does not reproduce actual conditions, particularly as related to temperature, sunlight, biological population, water movement, and oxygen concentration. Since both the COD and BOD procedures are time-consuming, total organic carbon (TOC) determination is often adapted to provide a speedy and convenient way of estimating the other two parameters that express the degree of organic contamination.(45)

Total carbon (TC) and TOC were determined for leachates from processed and unprocessed spent limestone and dolomite and fly ash from

Argonne and Exxon pressurized fluidized-bed units, along with a control leachate from a natural gypsum. A model 915 Beckman TOC analyzer was used. Results summarized in Table 25 verified the assumption that the organic content is extremely low or nonexistent. The TC and TOC values were near the limit of detectability for all the leachates and control analyzed.

Activity Tests

The activity of residual lime in spent sorbents and fly ash was determined by its heat release property on contact with water, as the hydration reaction of CaO is extremely exothermic.(46) This was done

TABLE 25. TOTAL INORGANIC AND ORGANIC CARBON IN LEACHATE FROM UNPROCESSED AND PROCESSED FBC SOLID WASTE

Sample	History	Total Carbon (ppm)	
		Inorganic	Organic
Exxon No. 19.6 Bed Material	Limestone, pressurized once-through, unprocessed	<7	<5
Exxon No. 19.6 Fly Ash	Limestone, pressurized once-through, unprocessed	<5	<14
Argonne C2/C3 Bed Material	Dolomite, pressurized once-through, unprocessed	<5	<16
Argonne LST-1 Bed Material	Limestone, pressurized once-through, unprocessed	<5	<5
Argonne CCS-10, Regenerator Bed Material	Dolomite, pressurized regenerative, unprocessed	<5	<5
Processed Compacts: I2C, I3C, I3D, I4C, II4C	Processed cubes by room-temperature blending of Exxon No. 27 spent sorbent and fly ash	<5	<5
Natural Gypsum	Control	<7	<8

calorimetrically. In a standard test 3 g of stone were added to 20 ml of deionized water in a Dewar flask which had been thermally equilibrated. Chromel-alumel thermocouples were used to monitor the temperature rise in the stone/water system with an Omega cold junction compensator and a millivolt recorder. The heat release tests were conducted on the actual spent sorbent and fly ash from the fluidized-bed combustion units. Calcined and uncalcined limestone and dolomite samples were also tested for comparison. Table 26 summarizes the maximum temperature rise when 3 g of a solid sample were added to 20 ml of deionized water. Results showed that the available batches of spent sorbent and fly ash did not give off heat spontaneously on contact with water. In cases where there was residual calcium oxide present, it might have been hydrated in air during storage, dead-burned during the process, or coated with impermeable $CaSO_4$ so that no spontaneous heat of hydration was detected. These results seem to indicate that no heat-release problem is to be expected as a result of the solid waste disposal from the once-through pressurized FBC process. One must bear in mind, however, that the compositions of the spent sorbent, and therefore the heat-release properties, differ with processing variations and operating conditions. The potential heat-release must be determined from the atmospheric spent sorbent, since the only sample available in this category was a PER sample from an unknown storage pile that had neither an identified sample history nor a "typical" sample composition.*

The presently used activity test procedure was established in our laboratories as a screening test to compare the residual lime activity of spent sorbent from different processing conditions. The solid/water ratio selected in the bulk range as specified by the ASTM C110(47) (76 g in 380 ml water) and work by Murray et al.(48) (lime:water being 1:7) was found empirically to provide much better repeatability than that from a

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*Since the date of the preliminary issuance of this report, several additional batches of FBC residue (AFBC and regenerative PFBC) have been made available for testing. The heat release property summarized in Table 27 reflects the up-to-date results.

TABLE 26. HEAT-RELEASE PROPERTY OF FBC WASTE

Sample, Solid/Waste (3g/20 ml)	ΔT_{max}, °C
Argonne C2/C3 spent dolomite	<0.2
Argonne VAR-4 spent dolomite	<0.2
Argonne REC-3 spent dolomite (3rd cycle combustor)	<0.2
Argonne CCS-10 spent dolomite (10th cycle regenerator)	<0.2
Argonne LST-1 spent limestone	<0.2
Argonne LST-2 spent dolomite	<0.2
Argonne LST-3 spent dolomite	<0.2
Argonne LST-4 spent limestone	<0.2
Exxon No. 8.4 spent limestone	<0.2
Exxon No. 27 spent dolomite/limestone	<0.2
Exxon No. 27 fly ash	<0.2
Exxon No. 19.6 spent limestone	<0.2
Exxon No. 19.6 fly ash	<0.2
Exxon No. 30.2 spent limestone	<0.2
Exxon No. 26 fly ash	<0.2
Exxon No. 34 fines	<0.2
PER spent limestone (atmospheric)	<0.2
Natural gypsum	<0.2
Tymochtee dolomite, -16 +18 mesh	<0.2
Limestone 1359, -18 +35 mesh	<0.2
Calcined limestone 1359, -18 +35 mesh	>55

higher solid/water ratio that would give greater magnitude of temperature rise but lack reproducibility, most likely because of local heating. The former procedure has been adopted because it is fast, it requires only a small quantity of stone, and its results reproduce well. The latter procedure (small quantity of water added to larger quantity of solid) is also planned, however, because it provides higher sensitivity and simulates rainfall onto the disposed solid.

CONCLUSIONS AND ASSESSMENT

Results from laboratory testing indicate that the spent sorbent and fly ash from the fluidized-bed combustion process can be disposed of directly as landfill. The design and construction of the landfill site should minimize leachate generation so that potential water contamination from calcium and sulfate ion dissolution and leachate alkalinity can be prevented.

Data from the laboratory-scale investigation of direct disposal of the FBC residues indicated that:

- Trace metal ions are not likely to be water-contaminating.
- The dissolved organic concentration is low and near the limit of detectability.
- Magnesium is not soluble, even from the spent dolomite sorbent.
- Sulfide will probably not be a problem for the once-through FBC system.
- Heat-release on contacting water decreases with the following order: AFBC bed → AFBC ash → PFBC bed, regenerative → PFBC bed, once-through → PFBC ash. Heat-release property from the AFBC residues may be an environmental concern which may be prevented by careful selection and design of the disposal site.
- Potential environmental concerns are: heat-release, leachate alkalinity, TDS, calcium and SO_4. Calcium and SO_4 from most FBC leachates are similar to those of natural gypsum leachate.
- The potential environmental impact from leaching can be improved by further processing.

Intermittent leaching results indicated that initial leachate characteristics were better from the spent dolomite sorbent, but the spent limestone leachate improved much faster with total leaching time or leachate volumes. Spent dolomite from the once-through system gave better quality leachate than did the regenerated sorbent. Preliminary results also showed that the spent sorbent from the atmospheric FBC process displayed leaching properties similar to those of the pressurized FBC sorbent. This is encouraging but should be confirmed with more typical spent sorbents from the atmospheric FBC process.

Results also show that the leachate of spent limestone bed material had higher pH, calcium, and TDS than did the corresponding leachate of fly ash. The leachate from fly ash is similar to that of natural gypsum, except for higher pH from the fly ash. The addition of $\geq$20 wt % fly ash to the spent bed sorbent improved the leachate quality so that it meets the gypsum criteria except for pH. This suggests codisposal of spent bed sorbent and fly ash generated from the fluidized-bed combustion process to minimize the environmental impact from the sorbent's leachability. The environmental impact from disposal is reduced further by room temperature processing -- in other words, spent FBC sorbent/FBC ash blending.

Since there are no criteria for leachates at the present time, results from the continuous leach test which represents the worst possible case are compared with drinking water standards and leachate characteristics for natural gypsum. As an indication of environmental acceptability, a preliminary comparison is presented in Table 27 for those categories of spent bed material and fly ash tested. The processed spent sorbent/fly ash compacts from room-temperature blending possessed similar and better leachate characteristics than did the unprocessed sorbent/ash mixtures, which in turn displayed better leachate quality than did the spent bed sorbent alone.

TABLE 27. PRELIMINARY INDICATIONS OF ENVIRONMENTAL IMPACT FROM THE FBC SOLID WASTE DISPOSAL

Sample	Process	Sorbent Type	Environmental Parameters							
			Heat Release*- Spontaneous Temp. Rise (3g/20 ml)	Trace Metal	Total Dissolved solids	Total Organic Carbon	pH	Calcium	Sulfate	Sulfide
Bed Material	Pressurized FBC, once-through	Limestone	<0.2°C		▩		▩	▩	▨	
Bed Material	Pressurized FBC, once-through	Dolomite	<0.2°C		▨		▩	▨	▨	
Bed Material	Pressurized FBC, regenerative	Dolomite	To be determined		▩		▩	▩	▨	To be determined
Bed Material	Atmospheric FBC, once-through	Limestone	To be determined		▩		▩	▩	▨	
Fly Ash	Pressurized FBC, once-through	Limestone	<0.2°C		▨		▩	▨	▨	
Mixture of bed material and fly ash (unprocessed)	Pressurized FBC, once-through	Dolomite/limestone	<0.2°C		▨		▩	▨	▨	
Processed Compacts from bed material/ fly ash mixtures	Pressurized FBC, once-through	Dolomite/limestone	<0.2°C		▨		▩	▨	▨	
Gypsum	Natural	—	<0.2°C					▨	▨	

*Based on results from limited samples available and subject to the procedures specified in the section on "Activity".

▩ Do not meet either the drinking water or gypsum leachate criteria

▨ Pass gypsum leachate criteria but not drinking water standards

☐ Pass both drinking water and gypsum leachate criteria

SECTION 6

OCEAN DISPOSAL

Sorbent, whether regenerated or not, must eventually be disposed of. Spent sorbent may well be utilized as a product raw material. Some spent sorbent, particularly from inland plants, will probably be disposed of in landfills. At some sites, however, it is anticipated that, as an alternative ocean disposal may be preferred or may even be necessary.

FEASIBILITY STUDY

The first of two studies, an investigation of ocean dumping feasibility, was completed in September 1976. This report entitled "The Feasibility of Ocean Dumping as an Interim Alternative to Disposal of Spent Stone from the Fluidized-Bed Gasification Process" is included in its entirety in Appendix A. This report presents the following information relative to ocean disposal of spent sorbent:

- Federal regulations and permit procedures; summary of EPA regulations and criteria
- Approved sites for ocean dumping
- Ocean dumping mechanisms; ocean dumping costs
- Feasibility of dumping spent stone at sea
    - Attitudes toward various disposal methods
    - Requirements under the established permit system
    - Description of the Westinghouse test program for measurement of solution characteristics, heat release, and chemical changes associated with ocean dumping of spent stone.

The test results led to the conclusion that because of the high pH caused by mixing the spent stone and [ocean] water, there may be synergistic effects or the formation of toxic compounds during the immediate release process. This matter must be clarified further before proceeding with a permit consideration.

This preliminary study clearly outlined the requirements for obtaining a dumping permit. Before continuing experimental dispersion studies and biotoxicity testing, a second investigation was conducted to sense the current attitudes toward issuing dumping permits and to identify specific testing requirements.

SURVEY OF CURRENT EPA ATTITUDE TOWARD OCEAN DUMPING

This study completed February 1, 1977, is attached as Appendix B. It is an assessment of today's practice in issuing permits and a projection of the probability of dumping spent sorbent.

The specific objectives of this assessment were to (1) determine EPA's attitude toward ocean disposal of sulfated and sulfided limestone in all contiguous U. S. EPA regions, with emphasis on Regions III and IV, (2) estimate the probability of EPA issuing an ocean disposal permit in calendar year 1977 and between 1978 and 1983, and (3) determine what preliminary bench-scale dispersion and biotoxicity test will satisfy current EPA requirements.

These three objectives were met by contacting EPA Regional Offices and research laboratories and reviewing rules and regulations as reported in the Federal Register. From these contacts and reviews it is concluded that obtaining a permit from EPA to dump waste on a commercial scale would be extremely difficult in either 1977 or between 1978 and 1983 because of EPA's general policy to phase out all ocean disposal of industrial waste by 1981. The feasibility of ocean dumping is further limited by the kinds of constituents associated with the waste and by the regulatory requirements to perform a detailed environmental assessment of the waste and to monitor the dump site.

TEST PROGRAM

The resistance to ocean dumping makes issuance of a permit seem improbable and discourages the appreciable cost of bioassays, chemical characterization, and dispersion analyses. A revised test program is being prepared which would permit an initial assessment of the environmental impact of disposal in the ocean and an assessment of ocean utilization as an alternative.

SECTION 7

UTILIZATION

Whatever the outcome of studies on direct disposal of FBC spent sorbent, a review of possible commercial uses for the large tonnages of solids involved was undertaken as an appropriate parallel effort. This review considered and developed several subjects, including a detailed look at potential markets, an estimate of the maximum investment in processing facilities, an examination of work in related areas, execution of bench-scale tests, and an assessment of utilization.

OPTIONS

An initial appraisal of the problem of spent stone disposition was given in Appendix F of the 1975 Westinghouse contract report to EPA.(36) This included consideration of the effect of variations in the FBC process itself, the production rate of spent sorbent and its chemical composition, governmental regulations, possible markets, and stone processing alternatives. It was apparent that only large markets should be evaluated. The acceptable final chemical forms for disposal to the environment would be carbonate, silicate, or sulfate. For dolomitic sorbents, magnesium would emerge as MgO. Should processing of spent sorbent prove necessary for either disposal or utilization, twenty-one alternatives were proposed. Possible end uses identified were:

- Soil stabilization
- Landfill
- Concrete/aggregate
- Gypsum

- Acid mine drainage treatment
- Municipal waste treatment
- Refractory brick.

These options remain attractive, although the work of the past year has led to assignment of higher priorities to those requiring a minimum of processing and, preferably, only low-temperature processing. Low-temperature fixation of the material is also of interest solely from the standpoint of reducing the leaching properties of the residue after disposal.

MARKET DATA

Primary Markets

When considering potential utilization of the spent sorbent, a prime consideration is the potential quantity of material to be generated. A 1000 MWe plant operating on a 3 percent sulfur coal will produce perhaps 570,000 Mg/yr of spent limestone or 450,000 Mg/yr of spent dolomite. Such quantities can only be utilized in some sector of the construction industry. This could mean landfill or road construction and, at upgraded levels of utilization, cement, concrete, and aggregate. Some statistics(49) are given in Table 28. The higher prices for aggregate (sand and gravel) appear to pertain to metropolitan areas that are exhausting local supplies of acceptable aggregates. Agricultural uses (liming, soil conditioning) might also be outlets for spent sorbent but are at a competitive disadvantage with limestone.

Special Markets

On the assumption that a concrete of sufficient compressive strength could be developed, three specific utilizations, in addition to use in general heavy construction, were explored. One is in coal mining, a second in low-cost housing, and the third in radiation shielding. These are discussed in the following paragraphs.

TABLE 28. MARKET DATA ON SELECTED CONSTRUCTION MATERIALS

Material	Million Mg/year	Price level ($/Mg)
Portland Cement	67.5	21.10-29.10
Masonry Cement	2.8	22.90-37.50
Quicklime	13.0	28.70-70.60
Sand	333	1.75-4.75
Gravel	495	1.80-4.95

The room-and-pillar method for underground mining of coal has the disadvantage of leaving about half the coal in the supporting pillars. On the other hand, mine disposal of solid wastes is economically unattractive in the United States because the transportation costs through miles of underground tunnels are too high. If recovery of coal from the pillars were made possible by the use of pillars made from spent sorbent, however, the combined disposal/recovery operation might prove economical.

Assuming square cross-sectional pillars of coal with side W are left under the present system, and the space between the pillars is aW, then the fraction of coal recovered is given by:

$$f = \frac{(1 + a)^2 - 1}{(1 + a)^2} ,$$

from which

$$a = -1 + (1/(1 - f))^{1/2} .$$

For the typical 50 percent recovery, a = 0.414. Since half the coal is removed, the compressive load on the remaining coal has been increased by a factor of 2.

If the coal has an average sulfur content of 3 percent and an ash content of 13 percent, and if the gasification or combustion processes use a limestone/sulfur treat ratio of 3:1, the amount of waste produced is 37.8 kg/100 kg coal. Adding water at the rate of 0.3 kg/kg of mix to produce a solid compact, the amount of waste returned to the mine is 0.49 kg/kg coal. If the density and compressive strength of the solid compact are comparable to those of coal in situ, such an application would be at least technically feasible.

Another possibility is low-cost modular housing. Assuming a 12 by 15 by 8 ft (inside dimensions) module with 6-in thick walls and plates, the module would require about 6.8 Mg of material. This allows for one door and four window cutouts per module. A 1000 MWe plant on limestone could generate material for about 120,000 such modules annually. Domestically, assuming a 1 percent population growth, the demand for dwelling units would be about 1,000,000/yr. At five modules/unit, the output of forty 1000 MWe power plants would be required. The potential in other parts of the world is considerably greater.

A further aspect domestically is the potential for radiation shielding either for industrial or residential use. Civil Defense activity has been at a low level for many years, after an initial flurry of concern. Strategic planning, however, could include the systematic conversion or modification of at least critical plants from conventional industrial designs to those that offer radiation protection from nuclear attack. The technology of concrete for such applications involves the use of such high-density aggregates as iron scrap, iron ores, barium sulfate, plus a higher water content. With a low-cost concrete, it may prove feasible to use thicker sections. At present, a concrete reactor shield for biological protection may be 10 ft thick. Water content is an important factor for neutron shielding. The presence of calcium sulfate should not be deleterious per se, since barium sulfate can be used. Iron oxide from coal ash should be advantageous, but the effect of trace elements would have to be determined.

Other Markets

Use of spent sorbent as a source of low-cost lime in applications such as acid mine drainage and municipal sludge treatment was not examined in detail during this reporting period. It is assumed, a priori, that this is technically feasible; what is needed is a sufficient quantity of spent sorbent to make a field test.

In the high-temperature area both cement and brick remain as possibilities, although it is expected that these would be at a competitive disadvantage with respect to low-temperature processes. Nevertheless, bench-scale tests were planned, at least for limestone-type sorbents, to explore cement production.

OVERALL ECONOMICS

A rough estimate can be made of the maximum capital investment permissible for sorbent processing. A suitable reference case is that of simple disposal, for which there will be some minimal investment in cooling facilities and, perhaps, storage capacity for a nominal period of 1 to 3 shifts. The major direct operating cost would probably be that of transporting the spent sorbent to a disposal site. Any alternative would involve some incremental capital investment over that for the reference case and either a lower operating cost or some incremental direct operating cost, plus a product realization.

If P_s is the selling price of a marketable product per Mg, and ΔC_p is the incremental production cost per Mg of spent sorbent, then the gross realization in the case of making a saleable product is $P_s - \Delta C_p$ \$/Mg. Since a 1000 MWe plant would produce about 450,000 Mg/yr of a sulfated dolomite, each \$/Mg realization would have the effect of reducing operating costs by \$450,000/yr. Assuming 17 percent capital charges, 48 percent taxes, and a 20-year life, the allowable incremental investment then works out to about \$890,000 per \$/Mg realization in selling price over incremental direct production cost. The cost includes utilities, chemicals, direct labor, and certain charges estimated on the basis of direct labor. This incremental investment would be recovered in 5 years through the realization. If it is argued that sorbent disposal is not intended to be a profit-making operation, a longer payout time can be used. For a 20-year payout time, the incremental investment would be about $2,060,000.

Since aggregate is selling for about $4.50/Mg, if the fly ash compacts were technically competitive, and therefore could command the same price, the processing plant obtained for a $1,000,000 incremental investment over simple disposal would have to have an operating cost of no more than $3.50/Mg. This would be lower if an economic incentive had to be provided to permit the compacts to enter the market. If the usual cost estimating factors apply, each $1/Mg realization would support a bare equipment investment of about $270,000.

These rough calculations support the view that it is at least marginally justifiable economically to invest in simple processing facilities for spent sorbent. It should be noted that all estimates of the economics of environmental protection are at a disadvantage compared to the do-nothing or the direct disposal cases since there is as yet no accepted figure for the cost of the environmental impact.

TECHNICAL REQUIREMENTS

Study of environmental aspects of spent sorbent disposition led to a recognition of the need to understand the nature of water pollution control, as well as the nature of aggregates and the characteristics of cement and concrete.

Environmental Considerations

Water pollution will, of course, be a consideration whether the final material is used as a landfill, a road bed, or in solid compacts exposed to the environment. To put this in an engineering perspective, such water pollution requires a series of events:

- There must be a source of water.
- The water must contact the solid.

- The substances subject to leaching must be in a chemical and physical condition such that leaching is possible.
- The contact time, contact temperature, and water/solid ratio must favor leaching.
- The leachate must be able to migrate to a water stream in sufficient quantity.

The addition of solutes to ground water supplies can therefore be controlled, or prevented, but perhaps not completely eliminated by appropriate action to modify one or more of these events.

With respect to water sources, omitting man-made sources as susceptible to control, the question is essentially one of management of precipitation (rain or snow). Such water either flows to its lowest level on the surface of the earth or permeates the earth, always flowing downward under the influence of gravity until it reaches an impermeable stratum such as rock or dense clay. If an underground aquifer does not develop, water will collect on the surface, forming a lake until it is deep enough to overflow the lowest point in its banks.

Thus, if one wishes to avoid water pollution by eliminating the water source, the site chosen for accumulation of the spent sorbent must be well above the local water table and must have more annual evaporation than precipitation. It is likely that neither of these conditions can be more than partially met for most power plant locations.

Whatever water is available at the site can still be prevented from contacting the spent sorbent. The site can be designed for maximum diversion of surface runoff from adjacent areas and for maximum runoff of surface water from the site itself. Ground water moving vertically under a hydrostatic head created by its sources can be diverted by bottom drains and liners. Earth movements and chemical reactions with the local soil, however, over many years can change the permeability of the soil to leachate from the spent solids. In addition, liner life is probably no more than about 20 years.

Even if some water contact cannot be prevented, the potential pollutants must be in a form that can be leached out by water. It is known that exposure to high temperature modifies the pore structure of solids like lime and gypsum so that they are considerably less reactive and are hence termed dead-burned. Further, other pollutants like sulfide or sulfate sulfur and trace elements may be contained within the solids and, therefore, may not be leachable except with long contact times. What this suggests is that a disposal pile might be designed for maximum porosity to permit any water falling on its surface to drain off as rapidly as possible. The effluent would, of course, have to be monitored.

Finally, if some leachate is produced, it can be collected and treated, since it presumably represents a much smaller amount of pollutant than that in the original solids.

Overall, this brief review indicates that one or more of several simple design features can be used effectively to control and minimize water pollution. Leachates must be managed to avoid more expensive corrective measures in subsequent years. Competition for disposal sites near population centers does exist, but this is a matter of long-term economics. The trade-off is the cost of mine-mouth power generation or even population dispersal versus the cost of transporting wastes long distances. Such a study is outside the scope of the present investigation but is considered relevant to the total solution.

Some researchers have been investigating the retentive capacity of clay soils for pollutants. Griffin(50) reported on the ability of mixtures of kaolinite, montmorillonite, and illite with sand to remove heavy metals as well as other substances from leachate from a Chicago landfill. Anaerobic conditions and long contact times, corresponding to a flow of less than 2 pore volumes per month, were used. Permeabilities were of the order of 10^{-6} cm/s for the pure clays and 10^{-3} for sand. Mercury, lead, zinc, and cadmium were strongly attenuated by the clays, with montmorrillonite being the least effective of the three. The capacity of the clays for heavy metal ions was low, however, as indicated by the range of 2 to 16 ppm for lead or kaolinite. This means leachates permeating soils will eventually saturate them, and a further influx of such ions will result in a breakthrough. Such findings favor immobilizing potential pollutants as a means of environmental protection in the event landfill is chosen as the disposal method.

The preceding considerations support the conclusion that a synthetic aggregate would offer the potential for immobilizing pollutants while avoiding the question of mass permeability. Some of the spent sorbent might be usable as fine aggregate, but fines would have to be screened and disposed of in a suitable manner. By pozzolanic reactions, either they or the entire spent sorbent might be converted into a coarse aggregate. A final possibility is to dispose of the spent solids in a landfill by casting essentially monolithic blocks. If the aggregate possibility is supported by test data, then the spent sorbents would be directed to road construction or concrete.

Characteristics of Aggregate

To aid in assessing the potential for synthetic aggregate, the basic characteristics of natural aggregate were reviewed. By definition(51) aggregate consists of uncrushed or crushed gravel, crushed stone or rock, sand, or artificially produced inorganic materials. For use in concrete, aggregate should be hard, durable, tough, strong, and clean, with only limited amounts of flaky or elongated particles, adherent coatings, or harmful materials. The terms gravel, stone, and rock appear to be used interchangeably, but they may be distinguished by size; in other words, stones are small rocks or fragments of rock and gravel consists of small rounded stones or fragments of stones.

Rocks contain one or more minerals, of which the more common are feldspars, ferromagnesians, micas, clays, zeolites, silicates, carbonates, sulfates, iron sulfides, and iron oxides. Chemically, the first five are silicates of aluminum, calcium, iron, or magnesium, with potassium and/or sodium present in some cases. What is of interest is the chemical reactivity and the physical structure. Clay minerals and zeolites show large changes in volume on wetting and drying. Sulfates, as in gypsum and anhydrite, offer the risk of attack on cement. Porous cherts, shales, some limestones, and some sandstones are known to be susceptible to frost damage. Chert is a very fine-grained rock composed of silica in the form of cryptocrystalline quartz, chalcedony, opal, or combinations thereof, and may be alkali reactive. Quartz is anhydrous, opal is hydrous, and chalcedony is believed to be a mixture of the two. Other known alkali-reactive constituents are tridymite, cristobalite, zeolites, heulandite, the glassy-to-cryptocrystalline rhyolites, dacites, andesites, and certain phyllites. The deleterious expansions sometimes do not occur until two or more years after the concrete is placed.

Unconsolidated sediments include gravel, sand, silt, and clay, according to particle size. There is, however, also a trend in composition. Gravel and coarse sands usually are rock fragments. Fine sands and silt are predominantly mineral grains. Clay consists exclusively of mineral grains, largely of the clay minerals group. On consolidation, sandstones, siltstones, and claystones are formed. The cementing material may be quartz, opal, calcite, dolomite, clay, iron oxides, or other materials. Hard, platy claystones are shales. Some shales cause concrete to fail because of excessive shrinkage. Dolomite in certain carbonate rocks is present as large crystals scattered in a finer-grained matrix of calcite and clay. Such a structure leads to deleterious expansions in concrete.

Micas are subject to cleavage and also may alter during the hydration of cement. Iron sulfides form ferrous sulfates that, in turn, yield iron hydroxide and calcium sulfoaluminate. Surface staining is also possible.

Characteristics of Cement and Concrete

Concrete has a variety of uses depending on its density, compressive strength, and durability. These properties depend, in turn, on the chemical nature of the cement used, the density of the aggregate, the cement and water content of the mix, the method of preparation of the concrete and the air content of the mix. Three main types of concrete may be distinguished.

Structural lightweight concrete aggregate is defined(52) as concrete having a 28-day compressive strength in excess of 17.2 MPa and a 28-day air dry weight not exceeding 1850 kg/m^3. Compressive strengths of 41.4 MPa are possible with lightweight aggregate. Low-density concretes from lightweight aggregate have compressive strengths in the range of 0.7 to 7.0 MPa and unit weights of 320 to 800 kg/m^3. Moderate strength lightweight aggregate concretes fall in between. Lightweight aggregate reduces the dead weight of a structure but usually costs more per cubic yard than ordinary concrete. A lower overall cost can be obtained through a lower volume of cement and reduced structural and reinforcing steel and lower forming and handling costs. The low-density concretes are used for insulation, and moderate strength concretes are often used as fill. The structural grade is used for high-rise buildings.

High-density concretes, with unit weights to 6010 kg/m^3 are used in radiation shielding. The high-density results from the type of aggregate used, but the water content is also a factor in effectiveness of neutron deceleration and capture.

Normal density concrete 1840 to 3200 kg/m^3 has a wide range of principally structural applications. It has compressive strengths in the range of 17.2 to 27.6 MPa, but strengths are affected by many factors, as noted above.

A cement is a material with adhesive and cohesive properties that render it capable of bonding mineral fragments into a composite whole.

In construction the bonded materials are stones, sand, bricks, blocks, and so on. The cements used for this purpose are based on compounds derived from lime and are mainly silicates and aluminates. Various kinds of cements as defined by ASTM(53) are shown in Table 29.

From these definitions it appears that all of these cements contain calcium silicates formed at elevated temperatures that in concrete are hydrated to a silicate gel plus free calcium hydroxide. The current development effort includes examining the properties of compacts made by hydrating a blend of coal fly ash and spent sorbent that has not been exposed to temperatures as high as those in a cement kiln. The nature of the hydration products has not yet been determined. An alternative is to expose such blends to various temperature levels: autoclaving under moderate steam pressure, processing below the sintering temperature, processing at the sintering temperature, and processing above the melting point.

State of the Art - Disposal/Utilization of Solid Wastes

Relatively little has been done on disposal/utilization of FBC wastes. In contrast, so much has been done in related fields that it is a major task to summarize the contributions to defining and understanding the problem of disposal or utilization of calcium-based wastes. These fields include flue-gas scrubbing, sulfate wastes, cement, concrete, and fly ash. Certain contributions have been singled out to help answer the following questions:

- What is the impact of a calcium-based waste on the environment?
- Can this impact be lessened by one or more techniques?
- If the waste is utilized, will the product have a potential impact on the environment?
- What properties can be expected of solid products made from calcium-based wastes?
- What is the effect of mix composition on field performance?

TABLE 29. DEFINITIONS OF VARIOUS KINDS OF CEMENT

Hydraulic Cement -	A cement capable of setting and hardening under water
Natural Cement - ASTM C10-73	A hydraulic cement produced by calcining a clay limestone containing up to 25% by weight of argillaceous material below the sintering temperature and then grinding to a fine powder
Portland Cement - ASTM C150-73a	A hydraulic cement produced by pulverizing clinker consisting mainly of hydraulic calcium silicates and usually containing calcium sulfate as an interground addition
Portland Blast Furnace Slag Cement - ASTM C595-73	An interground mixture of Portland cement clinker and granulated fine blast furnace slag in which the slag is between 25 and 65 wt % of the blend
Portland-Pozzolanic Cement - ASTM C595-73	A uniform blend of Portland cement or Portland blast furnace slag cement and fine pozzolan produced by intergrinding clinker and pozzolan or blending cement and finely divided pozzolan, in which the pozzolan is between 15 and 40 wt % of the blend
Slag Cement - ASTM C595-73	A uniform blend of granulated blast furnace slag and hydrated lime in which the slag is at least 60 wt % of the blend
Supersulfated Cement -	An interground mixture of 80-85 wt % granulated blast furnace slag with 10-15 wt % dead-burned gypsum or anhydrite and about 5 wt % Portland cement clinker
Masonry Cement - ASTM C91-71	A hydraulic cement for masonry construction containing one or more parts of Portland cement, natural cement, Portland-pozzolan cement, slag cement, or hydraulic lime, and, in addition, one or more parts of hydrated lime, limestone, chalk, calcareous shale, talc, slag, or clay

Such a review is also constructive insofar as it helps identify the kind of information still needed from an experimental program in order to formulate recommendations. A practical consideration in the current work was the delay in receiving adequate supplies of representative spent sorbents.

Sulfate Wastes

Smith et al.,(54) in work sponsored by the Federal Highway Administration, reported on the suitability of mixtures of fly ash, lime, and sulfate wastes for highway construction. This work closely parallels that planned under the present contract for the examination of the lime-sulfate waste sorbent from fluid-bed combustion and, therefore, is reviewed in detail. Following an optimization of the mix composition, the reaction products were characterized, engineering properties were determined, and aggregate production was studied. The study differs from the present one mainly in that fluid-bed combustion waste was not examined. Conclusions relevant to Westinghouse studies are summarized in the following paragraphs. First, the effect of calcium sulfate was explored using simulated wastes. Four hydrated limes from commercial sources were used, including both calcitic and dolomitic types. Four calcium compounds were used to simulate wastes: two gypsums, pure anhydrous calcium sulfate, and a pure calcium sulfite hemihydrate. Five low-carbon fly ashes were used, low carbon meaning 1 to 6 percent loss on ignition at 950°C. No rationale was given for why high fly ash contents were used in the mixes: 80 percent fly ash, 12 percent lime, and 8 percent gypsum.

Effect of Water Content on Compressive Strength

Three methods were used for adjusting the water content of the mixes: compaction, extrusion, and slump. The latter involved mixing in just enough water to produce a consistency comparable to a slump by a standard AASHTO test on concrete. The water content obtained was about 18 to 27 percent for the compaction method and 35 to 45 percent for the slump method. The range of values of compressive strengths for test specimens produced by compaction was 16.5 to 35.4 MPa, which was generally 1.3 to 3.5 times those for specimens produced by the slump method. Values for extruded specimens were closer to those for the slump method than to those for the compaction method. These results are in line with a commercial technique known as the Schokbeton method for producing high-density, low water-content, high-strength concrete by subjecting it to rapid, vertical oscillations without causing segregation of the aggregate.

Effect of Lime Type

The two limes used contained 0.7 and 33.4 percent MgO, respectively. In two-thirds of the cases, the calcitic lime yielded higher strengths than the dolomitic. Six of the results showed the reverse, and the remaining four were of about equal strength. Statistical analysis of the data showed that all main effects (lime type, calcium compound, fly ash source, and water content) and all interactions were significant at the 95 percent level. Apparently because a highway construction application was in mind, however, the analysis was done only for the 7- and the 28-day values. It would appear relevant to examine the long-term (91-day) results since it is probable that the optimum techniques for utilizing these waste materials have not yet been identified.

Effect of Type of Calcium Compound

For the compactible data only, after 28 days calcium sulfite and calcium sulfate were equivalent. This finding is of importance to the present work since it implies that conclusions from the work on FGD sludges, especially in the fixation work, might be directly applicable in the processing and disposition of FBC wastes.

Effect of Lime/Sulfate Ratio

Smith found that with the better fly ashes, that is, with the two which gave the highest early strength in the preceding tests, 28-day strengths were maximized by using a lime/sulfate weight ratio of 1:1.

Strengths dropped off sharply on either side of the maximum. Lime/sulfate ratios in the range of 0.75 to 1.25:1 yielded compressive strengths within 85 percent of the peak. These results are for the specimens produced by compaction. No explanation was given for the results. Chemically, the lime/silica mole ratios for these two sets of data were nearly identical (0.28 and 0.26). These ratios are very low compared to Portland cement in which the lime/silica mole ratio is 2:3. On the other hand, it appears very encouraging that strengths in the normal concrete range can be obtained with such low lime/silica ratios.

Effect of Fly Ash Content

For the same two fly ashes as above, there was a monotonic and rapid decrease in strength as this ratio was increased from 4 to over 11, achieved by increasing the actual fly ash content of the mixes from 83 to 95 percent. It appears unreasonable to expect mixtures containing as much as 95 percent fly ash to be effective in binding waste sulfates. These data may be interpreted instead to say that no more than about 85 percent fly ash should be used.

Effect of Sulfate Content

It was found that 10 to 20 percent gypsum in mixtures containing 3 to 5 percent lime would yield maximum compressive strength. In another study(55) addition of up to 50 percent gypsum on cement showed a linear increase in compressive strength. Smith found further that substitution of anhydrous calcium sulfate for gypsum did not change the strength at 28 days, explaining this on the hypothesis that the calcium sulfate hydrated to gypsum. Strengths at 7 days were higher with the anhydrous sulfate, suggesting that this was a more reactive form. In the case of fluid-bed combustion wastes, any sulfate present should be at least partially dead-burned and, therefore, less reactive. The question of longer term effects, however, such as gradual hydration, needs to be answered.

Effect of Portland Cement Content

Addition of Portland cement was found to be detrimental to strength. Fly ash and sulfate levels within each data set, were held constant, however, so that increasing Portland cement meant decreasing lime. Since Portland cement depends primarily on hydration of dicalcium and tricalcium silicates, it would appear that a more meaningful experiment would keep lime constant or even increase it at the expense of the fly ash. To be sure, there is a cost factor, but in the case of FBC wastes optimization of the process design might include a certain minimum amount of CaO in the spent sorbent before it enters the spent sorbent processing section.

Effect of Other Components

Other substances tested for their effect on compressive strength were impurities and accelerators. Aluminum sulfate at the 1 percent level was concluded to have no effect, but from the data it appears to have been associated with a decrease in strength both at 7 days and at 28 days. The lime used, however, was dolomitic, and the fly ash used already included 25 percent alumina. Ferric hydroxide at the level of 2.8 percent also resulted in weak mixes.

The small amount of alumina in normal Portland cement is believed to have no useful function other than to lower the melting point of the kiln feed to facilitate the sintering process.

X-Ray Examination

Characterization of the reaction products for selected mixes by X-ray diffraction showed that for the reference lime-gypsum fly ash mix, lime disappeared within 7 days of curing, gypsum diminished, mullite increased over 9 months, and ettringite appeared after 28 days. It was concluded that a new phase consisting mainly of a calcium sulfoaluminate was formed, but it was not positively identified as ettringite. New crystals were observed to grow from the fly ash surface into the pore structure and intertwined, which might be an explanation for the strength increases at early curing times. It was also found that at least 10 wt % ettringite had to be present before it was visible under X-ray diffraction.

Tests on Industrial Sulfate Wastes

Having explored the effect of calcium sulfate on the properties of fly ash compacts, actual industrial sulfate wastes were tested in fly ash formulations. These included three neutralized acid mine drainage samples, one titangypsum from extraction of titanium dioxide, one gypsum from hydrofluoric acid manufacture, one neutralized waste pickling liquor from steel manufacture and two FGD scrubber sludges. The reference mix, containing 5 percent lime and 95 percent fly ash, developed a compressive strength of 2.6 MPa (370 psi) in 28 days. The specimens were prepared by the compaction technique. In all of the mixes prepared with waste sulfates, the fly ash content was in the range 72 to 93 percent, while the lime was 1 to 11 percent.

Screening Tests for Compressive Strength

Only two of the acid mine drainage samples were tested, the third being omitted because its solids content was too low (and apparently could not be concentrated by mechanical techniques like centrifuging). Significantly different strengths were demonstrated: 2.6 to 2.8 versus 4.6 to 5.6 MPa (370-405 versus 660-805 psi). No explanation was given for this difference. The waste with the higher CaO and SO_3 content, however, gave the higher strengths. Both had about 8 percent alumina plus iron oxide in the waste. The steel pickling liquor waste had similarly low values of strength, 2.4 to 3.2 MPa (355-465 psi), at the level of 5 percent waste. At 10 percent, the strength dropped to 0.34 MPa (50 psi).

The two waste gypsums yielded strengths in the range 6.6 to 10.1 MPa (950-1470 psi). It may be of interest that the total of alumina and iron oxide for these wastes was low (2-4 percent). At 3.2 percent lime increasing the waste sulfate content to 25 percent for the hydrofluoric acid waste showed a trend of increasing compressive strength for specimens prepared by compaction, 7.9 to 10.1 MPa (1150-1470 psi).

The scrubber sludge from Kansas Power and Light, which had 5 percent SO_3 (presumably sulfate sulfur) and 28 percent calcium as CaO, also showed a trend of increasing strength, with increasing waste content to 13 percent from 6 percent, 12.4 versus 6.3 MPa (1180 versus 920 psi).

The maximum compressive strength obtained was with a sulfite scrubber sludge from Louisville Gas and Electric, containing 68 percent solids and 4 percent sulfur as SO_3 and 32 percent calcium as CaO. The 28-day strengths were 10.2 and 12.3 MPa (1480 and 1790 psi). It was found that, unless mixing was adequate, pockets of unmixed sludge would be found in the compacted samples. The highest strength corresponded to the mixing technique in which the lime and fly ash were preblended and slowly added to the mixer containing the sludge and mixing water.

Engineering Evaluation

Six lime-fly-ash-sulfate formulations were used to make an evaluation of engineering properties like freeze-thaw resistance, wetting and drying resistance, California bearing ratio, permeability, splitting tensile strength, and leachability. Again, lime was never more than 5.6 percent of the mix; and the lowest fly ash content used was 62 percent, with four of the six mixes prepared in the range of 80 to 86 percent fly ash. Only calcitic lime was used in these mixes. A gypsum mix was used as the reference mix.

Effect of Aging on Strength. All of the mixes showed an improvement in strength properties on aging to 91 days. The standard developed as much as twice the unconfined compressive strength as the other five test mixes, 15.8 to 7.6 MPa (2295 psi versus 1100) and developed two to three times the splitting tensile strength, 3.6 MPa versus 1.1 to 1.6 MPa (520 psi versus 165 to 225 psi). Its CBR was 617 in 28 days versus 335 to 487 for the other mixes.

These values are all higher than that of the well-graded crushed stone CBR standard.

Effect of Mix Type on Permeability. In some cases, the permeability for the test mixes was lower than that for the reference mix, reaching values as low as 0.8 x 10^{-6} cm/s in 28 days. One of the scrubber sludges, Kansas PBL sludge, had a permeability of 17.0 x 10^{-6} cm/s. To put this in a more direct perspective, a permeability of 1 x 10^{-6} cm/s means that at steady state, leachate production would be 0.6 cc/min/m^2. It appears that acceptably low values of permeability can be achieved with fly ash/sulfate sludge mixes.

Samples cured for 28 days had generally much less solute leached than at 7 days, reaching concentrations in the range of 0 to 50 ppm of sulfate for some samples. It was concluded that lime and gypsum had reacted chemically to form insoluble material and that, considering the low levels of permeability achieved, ground water infiltration by leachates from these mixes would be very small.

Effect of Freeze-Thaw Exposure. In the freeze-thaw tests, it was found that 7 days curing was insufficient, since only one sample besides the reference mix survived 12 cycles. Wetting and drying proved to be less severe than freeze-thaw exposure. Curing for 28 days before freeze-thaw exposure yielded terminal values of compressive strength of the order of 2.1 MPa (300 psi).

These results are not favorable, but nor are they considered applicable to Westinghouse studies since the mix composition was at a much higher level of fly ash.

Aggregate Properties

Two formulations were also prepared, using somewhat more lime (7.5-8.0 percent), which were then cast or extruded to form solid specimens for testing as aggregate. After 28 days of moist curing, the mixes were still too soft for use. Curing for 14 days at 40.9°C yielded one usable material. This was crushed and graded. At least 10 percent fines were produced, in this step, that would in commercial operation represent waste that might not be recyclable or usable in some other way. The specimens failed the freeze-thaw, the sulfate soundness, and the Los Angeles abrasion tests. When made into a concrete with Type II Portland cement and an air-entraining agent, 28-day strengths up to 23.1 MPa were obtained. Again, all six beam samples tested failed the AASHTO T-161 freeze-thaw test in less than 104 cycles. It was concluded that none of the mixes yielded aggregates suitable for concrete subject to freeze-thaw conditions. Lime-fly-ash-waste-sulfate mixtures, however, might be suitable for road construction as base course, subbase, or embankment material. Longer curing times, of the order of 6 to 9 months, should produce stronger and more resistant aggregate particles. The effect of curing time specifically on freeze-thaw durability should be investigated.

Fly Ash

Dunstan,(56) in work done through the Bureau of Reclamation, concluded that, although lignite and subbituminous fly ashes would make concrete with satisfactory freeze-thaw durability and adequate compressive strengths, they should not be used where a severe sulfate condition, as defined by the Bureau's standards, exists. Fly ash characteristics found are summarized in the following paragraphs.

Composition

None of the five fly ashes tested met all of the requirements for Federal Class F pozzolans.

Dunstan noted that fly ash from the lower rank coals generally had lower Fe_2O_3 contents in the glass fraction, which typically is in the range of 60 to 70 percent. The glass fraction is considered the most reactive portion of the fly ash. Iron oxide appears to have a moderating influence on the formation of ettringite which, in turn, is mainly responsible for deleterious expansions. Fluidized-bed combustion fly ash, on the other hand, is formed at much lower temperatures than is normal fly ash, and the glass content can be expected to be lower. It is not necessarily less reactive because the lower temperature of formation may result in less change in pore structure.

Other properties of these low-rank fly ashes also differed from the requirements of Class F pozzolans. The total of $SiO_2 + Al_2O_3 + Fe_2O_3$ for all three lignite ashes and one of the subbituminous ashes were less than the 75.0 percent required. These same four ashes also had MgO in excess of 5.0 percent. Two of the lignites and the other subbituminous ash had specific surface areas less than 6500 cm^2/cm^3. It was not established that these variations were responsible for the differences in 7-day strength of a standard lime-pozzolan mix and alkali reactivity.

Compressive Strength

When mixed with sand, cement, aggregate, water, and an air-entraining agent, the 7-day strengths were in the range of 10.4 to 18.9 MPa (1510-2470 psi) versus 17.9 MPa (2600 psi) for a mix containing no fly ash. Compressive strengths continued to increase on aging for 180 days to the level of 31.1 to 39.0 MPa (4510-5650 psi) versus 41.0 MPa (5940 psi) for the mix without fly ash. At 365 days, the corresponding values were 32.3 to 41.5 MPa and 38.6 MPa (4680-6020 and 5560 psi), respectively. Dunstan pointed out that the fly ash mixes had less total cementitious material (cement + fly ash) than did the fly ash-free mix. Somewhat lower compressive strengths for the fly ash mixes were therefore not unexpected.

Linear Expansion

Mixes with 25 percent replacement of cement by fly ash generally showed larger expansions due to sulfate attack than did those with only 15 percent replacement. The reference fly ash, a Class F pozzolan representing a blend of six bituminous coal fly ashes from the Chicago area, showed about the same linear expansion at 15 and 25 percent fly ash. Continuous soaking in 10 percent sodium sulfate at room temperature produced expansions of 0.01 percent in 460 days. In an accelerated test consisting of cycles of 16 hours soaking in 2 percent sodium sulfate and 8 hours drying at 54.4°C, the expansions in the same length of time were about double (0.019 percent). In all other cases, including the no fly ash mix, greater expansions were obtained in less time, some nearly to the point of failure (0.5 percent).

This indicates a need to identify the cause and whether higher Fe_2O_3 content will be effective in reducing these expansions. Until these expansions can be controlled, the use of lignite and subbituminous fly ashes in cement-type products will not be possible.

STATE-OF-THE-ART SPECIFICATIONS AND TEST METHODS

Before a new material can become commercially acceptable, it must be standardized to the extent of meeting specifications on important characteristics as shown by particular tests. It appears that not only are there no specifications on FBC solids or products made from them, but there are also no directly applicable tests. In anticipation of adapting existing tests, such as ASTM-C666, to the FBC program, work done by others on freeze-thaw resistance and the more general question of test methods is presented in the next two sections.

Freeze-Thaw Resistance

Backstrom(57) investigated the effect of water-cement ratio on the freeze-thaw resistance of non-air- and air-entrained concrete. He concluded that the freeze-thaw resistance varies inversely with the water/cement ratio of the concrete. For non-air-entrained concrete with a water/cement ratio less than 0.45, the increased resistance is probably due to a decreasing amount of freezable water in the cement paste, which approaches zero at a ratio of 0.40 or less. For air-entrained concrete, the air void spacing varies directly with the water-cement ratio, and the freeze-thaw resistance varies inversely with the air-void spacing. This parameter is defined in ASTM C457(52) as the maximum distance of any point in the cement paste from the periphery of an air void. The spacing factor for the specimens used were in the range of 0.10 to 0.23 mm. Air voids reduce the strength of concrete but increase its durability. Cordon(58) notes that the protective action is obtained when the spacing factor for the air-void system is 0.20 mm or less. There are several kinds of pores and voids in concrete:(59)

- Gel pores - the interstitial cavities between the particles of tobermorite ($CaO \cdot SiO_2 \cdot H_2O$) and other calcium silicate hydrates, averaging 0.0015 to 0.0020 μm
- Capillary pores - the unfilled spaces between aggregations of gel particles formed by uncombined water in excess of that required for hydration and averaging 0.5 μm in diameter
- Bubbles of entrained air averaging from a few microns to a few millimeters in diameter.

Water in gel pores in concrete below 0°C is supercooled but not frozen until, perhaps, -78°C. Water in capillary cavities will freeze since the cavities are large enough to accommodate a sufficient number of molecules to make ice crystals. Bubbles of air are ordinarily not filled with water unless saturation has been brought about by vacuum or pressure. The basic mechanism of deterioration of concrete, and presumably of any solid body under freeze-thaw conditions, is the formation of ice in voids insufficiently large to contain them and insufficiently connected to the neighboring voids to permit excess water to escape or the ice to expand into them. Pressures are then developed in excess of the tensile strength of the cement paste.

In order to cure concrete so that it develops its maximum strength, sufficient water for hydration must be present within the mix and at the the boundaries of the mix. This can be provided by moist coverings, fog cure, or immersion. On the other hand, it appears detrimental to use conditions leading to saturation of all voids. It is, therefore, an objective in the development of a cementitious material to determine optima for particle size distribution, water content, and air content. Backstrom's work(57) did not cover the effect of air voids on sulfate resistance.

Standard Tests and Specifications

Another area of investigation is that of test methods and specifications. Brown,(60) in a paper dealing with energy conservation, concluded that a lack of standard tests and specifications was an important factor inhibiting the use of blended cements to perhaps 1 percent of the domestic market, whereas in France it is 60 percent. The industrialized countries use 20 to 30 percent blended cements.

ASTM C595-74, for example, covers three types of blended cements containing 15 to 40 percent fly ash, or 25 to 65 percent blast furnace slag or a minimum of 60 percent slag. Other compositions are not covered, so there is no basis for evaluating their suitability. The specification, however, includes six chemical tests and ten physical tests which may be unnecessarily restrictive. The fly ash specification C618-73 effectively excludes many western coal ashes on the basis of their total SiO_2, Al_2O_3, and Fe_2O_3 content, even though use of fly ash not meeting the minimum total of these constituents has not been shown to produce unsatisfactory cements. This specification also includes six chemical tests and thirteen physical tests. With regard to standard tests, Brown believes that new or improved tests are needed, including soundness, sulfate resistance, and freeze-thaw durability. The present test for soundness is intended to show whether the hydration of any dead-burned CaO or MgO in the cement after the cement has hardened will cause failure through excessive expansion. To get results in a reasonable time, an autoclave procedure is used in an effort to accelerate the hydration rate. This may be overly severe for Portland cement and inadequate for blended cements. Another objection is directed at testing specimens after only one day of curing. It is argued that this biases the results against fly ash cements because their one-day strengths are normally lower than those of Portland cement.

The only standard sulfate resistance test available is ASTM C452-68, which deals with the expansion of mortar and is applicable only to Portland cement. The description of the method also states that the method is intended for research on methods of determining sulfate resistance. Brown points out that the test procedure is not representative of field conditions. Gypsum is mixed with cement and then water is added. It is likely that adverse reactions can occur under these conditions before the mortar has developed its full strength. In the field, sulfate attack probably occurs by diffusion into the concrete after it has undergone substantial hydration.

Brown's objection to the ASTM C666-73 freeze-thaw test is similar to that for the soundness test -- namely, testing after a short curing period. In this case, the curing time specified is 14 days, although other times are permitted. This may not be an important objection in the case of FBC sorbents because strengths in the range 6.9 to 13.8 MPa (1000-2000 psi) within 7 days have already been demonstrated. The test has not been correlated with field performance quantitatively, however, so service life cannot be predicted. It would appear that the effect of curing time before subjecting to freeze-thaw testing should be included in testing new materials.

EXPERIMENTAL PROGRAM

Actual tests devised reflected the constraint of delay in spent sorbent supply. Pilot units were operated to yield data on the FBC process itself; thus, production of spent sorbent and associated fly ash were generally incidental aspects of the test runs. Within this constraint, the test program identifies the sorbents to be included, feasibility tests, and more extensive screening tests.

Identification of Spent Sorbents to Be Tested

Combustor Variables

The spent sorbent from fluid-bed combustion is basically a new material whose physical and chemical properties must be defined by appropriate tests. Examination of the main process as discussed in an earlier section reveals that at this stage of development there are still several potential spent sorbents to be characterized. The sorbent may be a limestone or a dolomite, or a synthetic based on these or on a different metal atom, such as iron. The spent sorbent is exposed to elevated temperatures for several hours and has a variable sulfur burden, which for calcium-based sorbents is in the form of calcium sulfate, possibly with traces of calcium sulfide. The balance of the calcium is expected to be principally a mix of calcium oxide and calcium carbonate, depending on the operating pressure and temperature. It is possible that some of the calcium may enter into reactions with the coal fly ash to form calcium silicates or aluminates. Trace elements from the fossil fuel and from the fresh sorbent will also be present. The physical structure of the sorbent will be modified by chemical reactions, pore migration, and pore size changes.

Further variations enter through other process conditions. The calcium/sulfur molar treat ratio will depend on whether the process is once-through or regenerative, the sulfur retention required, and the calcium utilization obtainable. For limestone once-through the ratio may be in the range of 1 to 5 for 90 percent sulfur retention. For dolomite the range may be somewhat narrower. For regenerative processes the range is projected as 0.2 to 2.0. The number of potential calcium-based sorbents to be characterized is estimated as follows:

• Two sorbent types	Limestone or dolomite
• Three molar treat ratios	Normal, high extreme, low extreme
• Three $CaO/CaCO_3$ ratios	Normal, high extreme, low extreme
• Two coal types	Reflects the $SiO_2/Al_2O_3/Fe_2O_3$ content of the coal ash
• One temperature level	One is probably representative

This leads to 36 different spent sorbents, that must be taken into account by the spent sorbent test program. It is expected that the sorbent properties relevant to disposal will not all be critical; thus, the actual number to be tested should be substantially less than 36. The manner in which this was handled is tested in the next paragraph.

Composition Ranges

To define the spent sorbent composition range of interest, Figure 24 was prepared with the aid of information reported in Appendix D of Reference 35 on sulfur retention in the fluidized-bed combustor versus calcium/sulfur mole ratio. The temperature selected was 850°C. The projected percent sulfur retention versus calcium/sulfur mole ratio of 850°C is:

Ca/S	Percent Sulfur Retention
1.0	50
2.0	80
3.0	95
5.0	98

The sorbent was 1359 limestone. It is not intended to imply that these values are definitive (since they are based upon laboratory TGA data at limited conditions), merely that they are representative. Ideally, 90 percent retention will be achieved at Ca/S = 1.0, in which case the spent sorbent will be mostly $CaSO_4$. Although the graph shows only three components, the calculations include an allowance of 5 percent for non-calcium impurities in the limestone. The parameter reflects the effect of varying degrees of calcination of the unreacted $CaCO_3$.

Based on available pilot-plant data, a representative composition, on an impurity-free basis is 63.3 wt % $CaCO_3$, 28.4 wt % $CaSO_4$, and

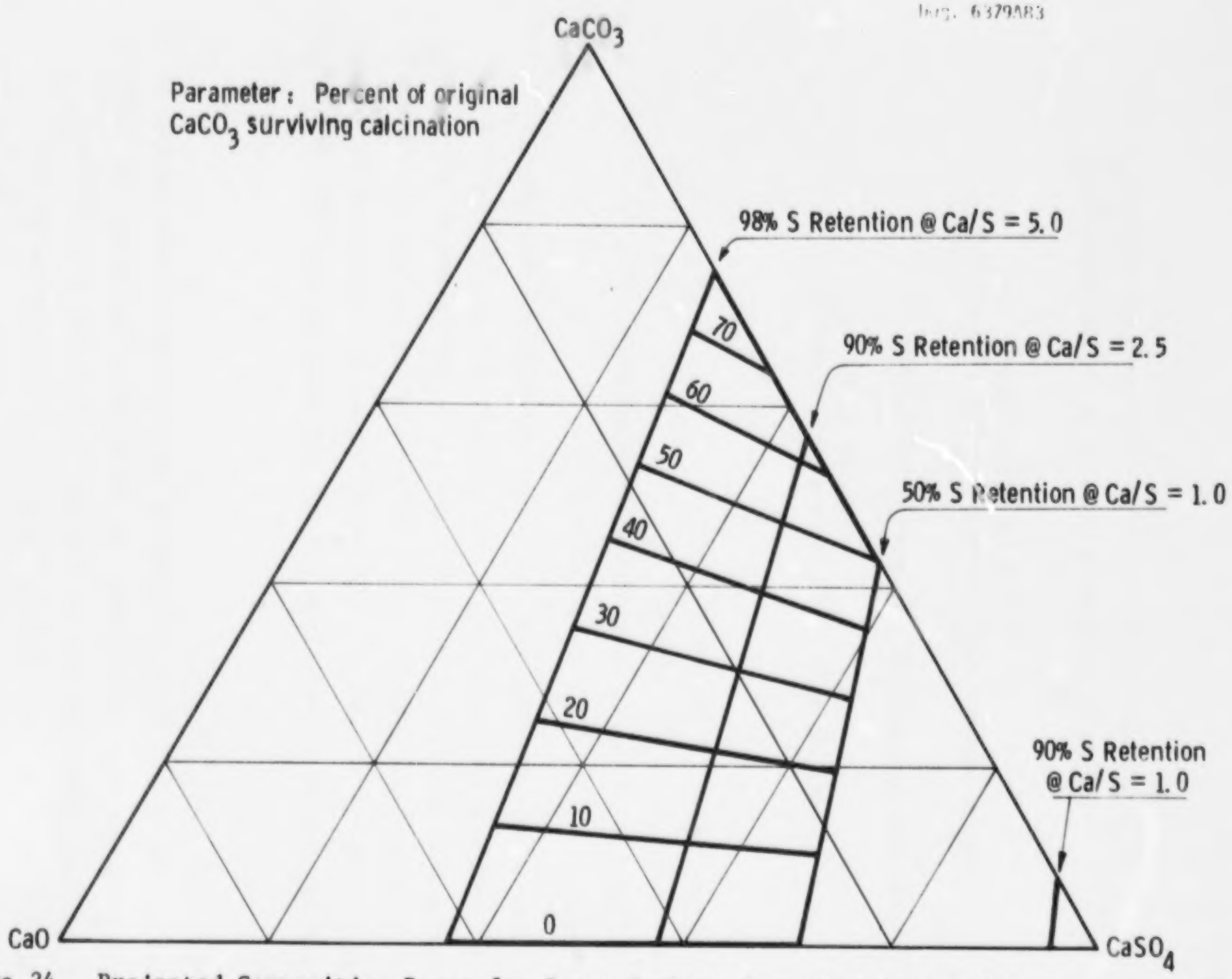

Figure 24. Projected Composition Range for Spent Sorbent from Fluidized Bed Combustion at 850°C

8.3 wt % CaO. Table G.1 of the same report shows the calcium/sulfur ratio used was 1.67.[38] The equations defining the system are:

Weight percent $CaSO_4$

$$= \frac{136.14\ a_s}{80.06\ a_s + R\left[56.08 + 44.01\ a_L + 100.09\left(\frac{1-f_L}{f_L}\right)\right]} \times 100$$

$$\text{Weight percent CaO} = \frac{56.08\ [(1-a_L)R-a_s]}{D} \times 100 \quad ,$$

where D is the same denominator as in equation 1; and

$$\text{Weight percent } CaCO_3 = \frac{100.09\ a_L\ R}{D} \times 100 \quad ,$$

where

R = molar treat ratio, Ca/S

a_s = fractional sulfur removal

a_L = fraction of $CaCO_3$ feed surviving uncalcined

f_L = fraction of $CaCO_3$ in feed limestone.

Solving these simultaneously with the above composition, including f_L as 0.9218, yields R = 2.2, and a_s = 50.2 percent and a_L = 60.9 percent. The latter checks out fairly well, but the other two values do not. As data are located and processed, they will be used to confirm the area of interest shown in Figure 24. Obviously, adequate quantities of spent sorbent of the proper compositions are not yet readily available for testing.

Sources

Upon review of available information on pilot-plant operations, it was decided to use the sources shown in Table 30 to represent the various FBC options. Chemical analyses of actual material used are in Table 31; B&W stone is included for comparison in anticipation of

TABLE 30. SPENT SORBENT TEST COMPOSITIONS

	Fluidized-Bed Process Type		
	Once-through Combustor	Once-through Boiler	One-Step Regenerative Combustor
Pressure	Atmospheric	Pressurized	Atmospheric
Sorbent	Limestone	Dolomite	Limestone
Projected Composition, wt %			
$CaSO_4$	43.7	64.1	26.1/43.1
CaO	54.0	6.6	70.1/54.6
CaS	-	-	1.3/0
MgO	-	28.1	-
Balance	2.3	1.2	2.5/2.3
Expected Sorbent Source	PER	Exxon	Not available
Actual Sorbent Composition, ash-free basis, wt %			
$CaSO_4$	69.4	61.2	-
CaO	30.6	22.6	-
MgO	-	16.2	-

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[a] Spent sorbent from regenerator/combustor.

future tests. Table 30 shows the PER stone is more sulfated than expected while the Exxon stone is close to target. The actual free CaO content is not known because of its possible chemical combination with oxides in the ash.

TABLE 31. CHEMICAL ANALYSES OF FBC SPENT SORBENTS

Source Material	Typical Duquesne Fly Ash (Conventional)	PER Bed	Exxon		B&W Run 19 Bed
			Run 43 Bed	Run 43 Fly Ash	
Composition, wt %					
CaO	0.40	28.84	38.64	15.62	67.01
MgO	1.0	2.13	13.25	7.70	1.25
SiO_2	44.9	27.20	8.60	29.40	3.90
Al_2O_3	19.1	10.26	5.70	11.20	5.55
Fe_2O_3	9.6	5.39	3.95	8.80	2.00
SO_3	--	19.90	29.00	16.38	19.09
LOI	14.0	1.04	0.32	4.23	0.51
Other	11.0	5.27	0.44	6.67	0.69
	100.00	100.00	100.00	100.00	100.00
Composition, moles/100g					
CaO	0.0071	0.5142	0.6890	0.2785	1.1949
MgO	0.0248	0.0528	0.3287	0.1910	0.0310
SiO_2	0.7472	0.4526	0.1631	0.4893	0.0649
Al_2O_3	0.1873	0.1006	0.0559	0.1098	0.0544
Fe_2O_3	0.0601	0.0338	0.0247	0.0501	0.0125
SO_3	--	0.2486	0.3635	0.2046	0.2384
Molar Ratios					
SO_3/CaO	--	0.4835	0.5276	0.7346	0.1995
CaO/SiO_2	0.0095	1.1361	4.8148	0.5692	18.4114
CaO/MgO	--	--	2.0951	1.4581	--

Feasibility Tests

Blending Tests

Experimental work began with bench-scale feasibility tests, making solid compacts by blending with fly ash. Using available materials, 4.4 by 4.4 by 2 cm blocks were cast from mixes containing Duquesne Light Company fly ash (from a conventional coal boiler) and oxidized sulfided Tymochtee dolomite made in the Westinghouse 10-cm laboratory test unit in Run D-1. The latter contained 28 wt % $CaSO_4$. The spent sorbent was ground to -125 μm. Compressive strengths given in Table 32 were normal to the 4.4 x 4.4 faces. These showed that the addition of 10 to 20 percent fly ash with or without Type I Portland cement yields compacts with significant compressive strength within 5 days' curing time. By way of perspective, a dense clay is perhaps the poorest soil considered suitable on which to erect buildings. It has an allowable bearing strength of at least 192 kPa. The cubes without Portland cement had a compressive strength of about 1380 kPa.

TABLE 32. COMPRESSIVE STRENGTH OF SULFATED DOLOMITE/FLY ASH BLENDS

	Composition (g)				Compressive Strength (5 days)	
Test	Sulfated Dolomite	Fly Ash	Type I Portland Cement	Water	MPa	psi
1A	100	20	--	76	1.59	230
1B	100	10	--	70	1.17	170
1C	100	20	10	80	2.21	320

When Exxon spent sorbent from the miniplant became available, its pozzolanic activity was tested. Five-centimeter cubes were cast from mixes of the spent dolomite from miniplant run 27(61) (refer to EPA-600/7-77-107) and the associated "fly ash" collected in the miniplant cyclones. The latter actually is a mixture of dolomite fines and coal fly ash. The spent sorbent was ground to -125 μm and two cubes of each of the two mixes prepared as shown in Table 33.

These values were considered very encouraging, especially since the MgO content was high. Mix 2 can potentially be used for low-grade structural production, i.e., continuously supported beams. The Mix 2 specimens weakened somewhat at 21 days, but at 28 days were back to the level of 7-day strength (9.33 MPa or 1352 psi).

TABLE 33. COMPRESSIVE STRENGTH OF 5-CM CUBES CAST FROM EXXON RUN 27 SPENT SOLIDS

Composition (g)	Mix 1	Mix 2
Pfizer 1337 spent dolomite	765	1080
Fly ash from miniplant	425	120
Fly ash, wt %	36	10
Water	530	360
Compressive Strength (7 day)		
Psi	355, 383	1405, 1325
Average (psi)	364	1365
(MPa)	2.51	9.41

Chemical analyses showed that, although the $CaSO_4$ and CaO contents of the spent sorbent were approximately as desired, the Ca/Mg ratio was about 2:1 instead of the expected 1:1. The interpretation was that the material received from Exxon was probably from an early part of Run 27 and limestone that had served as the start-up bed material had not been completely purged from the bed. The inert content was estimated from chemical analyses for sulfur, magnesium, CO_2, and H_2O as 38 percent, so the bed apparently retained a substantial amount of fly ash. The fly ash taken overhead had a Ca/Mg mole ratio of about 1.

Isostatic Pressing

An exploratory experiment was made on another portion of Exxon run 27 spent sorbent that had been ground to -125 μm. A cylindrical specimen was prepared dry, with no fly ash, by isostatic compression at 138 MPa (20,000 psi) for 1 to 2 minutes. The specimen was cured in water for about 2 weeks and then cut into four segments with an L/D ratio of 1 and the axial compressive strengths determined. Values obtained were 27.8, 40.1, 30.8, and 4.98 MPa (4040, 5822, 4472, and 7222 psi).

Follow-up data on this technique for three samples cured for about 40 days showed an average compressive strength of 89.3 MPa (12,960 psi). For comparison, normal Portland cement will yield values in the range of 103.4 and 172.4 MPa (15,000-25,000 psi).

These feasibility tests showed that:

- Stable solid compacts could be made at ambient temperature by blending spent sorbent with fly ash and adding water.
- Significantly high values of compressive strength could be achieved relative to the landfill requirements.
- At least for the curing times tested, MgO did not interfere with the pozzolanic reactions.
- Strengths higher than normal concrete are attainable by isostatic pressing. The strengths approach those of Portland cement cylinders made by isostatic pressing.

Screening Tests - Exxon Stone

It having been demonstrated that stable compacts could be produced even with a dolomite sorbent, prior to undertaking studies of engineering properties and durability, a screening test was designed to explore the effect of mix composition, water content, and curing time on compressive strength, response to leaching (which is reported elsewhere in this document), and compressive strength after leaching. Three mix compositions were chosen to reflect typical production proportions of spent bed material and fly ash, a low fly ash content, and an intermediate level of fly ash. The low was chosen arbitrarily at 10 percent, and the intermediate level was set 50 percent higher. Processing variables included fly ash/spent sorbent ratio, water/total solids ratio, particle size range, and free CaO/SiO_2 ratio. In these tests no CaO was added, and the spent sorbent was in every case ground to -125 μm.

As an incidental aid in planning tests, the predicted spent sorbent/fly ash weight ratio as a function of the sulfur content of the fuel and the calcium/sulfur molar treat ratio was developed (Appendix C, Figure C-1). Projections are based on 10 percent ash in the fuel, 90 percent retention of fuel sulfur, and the impurities in the sorbent. The ratio varies directly with the sulfur content of the fuel and inversely with the ash content of the fuel. For dolomite, the calculations predict 1.8 kg of spent sorbent will be produced per kg of coal ash from a 2 percent sulfur fuel at a calcium/sulfur treat ratio of 2, or 0.346 kg ash/kg sorbent + ash. These conditions appeared to be reasonable estimates applicable to Exxon run 27 material. Chemical analyses are given in Table 31 for the Exxon residues and for other residues used in this program.

The three fly ash contents chosen were 10, 35.8, and 15 percent, corresponding to low, typical production proportions, and intermediate levels. Two water contents were used, 44.5 and 30.0 percent, with a few observations at 34.2 percent. A minimum of three curing times was used: 7, 28, and 60 days. Duplicate samples were prepared in most cases. A parallel set of samples was made to be subjected to leaching for 1040 hours after curing for various lengths of time and then tested for compressive strength. The data obtained are presented in Table 34 and Figures 25 through 28, from which the following observations are made:

1. Significant compressive strength (at least 3 MPa or 435 psi) can be developed with mixes containing 10 to 36 wt % fly ash.

2. Most of the mixes developed 75 percent of their apparent ultimate strength within 7 to 10 days.
3. At 30 days of curing time, Mix III with 15 percent fly ash was 35 percent stronger than Mix II with 10 percent fly ash. Mix II was 2.5 times stronger than Mix I, which had 35.8 percent fly ash. All these contained 30 percent water. These trends persisted at 60 days of air curing time.
4. At higher fly ash contents (36 percent as in Mix I), the trend of the data in Figure 25 suggests the existence of an optimum water content. This is supported by the crossplot in Figure 28, where the optimum for 36 percent fly ash mixes is about 35 percent water. Similar optima are postulated for the other two mixes.
5. Leaching for 1040 hours appears equivalent to water curing. From Figure 25 strengths equivalent to that for the optimum water content (34 percent) were obtained by leaching specimens containing 45 percent water for 1040 hours. This suggests that it is preferable to have somewhat more water than optimum in order to have sufficient plasticity in the mix and then achieve the desired strength by adequate water curing.

Screening Tests - PER Stone

A 55-gallon drum of spent bed material was received from Pope, Evans and Robbins (PER). This was produced by burning Sewickley coal with Greer limestone at 815°C. Chemical analyses in Table 31 show that the calcium was about 48 percent sulfated. This was not a typical sulfation level but did offer an opportunity to test a spent sorbent at the high end of the sulfation range. Free CaO/SiO_2 works out to 0.6 on a molar basis. Initial results obtained for 2-in cubes with this material are shown in Table 35.

These tests were an exploration of processing PER as received. PER-1 showed that merely adding water does not result in significant cementitious reactions. Tables 36 and 37 provide possible explanations

TABLE 34. MATRIX FOR SCREENING TEST USING 2-INCH CUBES MADE FROM SPENT SORBENT AND FLY ASH FROM EXXON RUN 43

Mix	Sample	Fly Ash/ as % of Total Solids	Water/ as % of Total Solids	Nominal Curing Time (days)	Test	Date Cast	Compressive Strength		Actual Age at Test (days)
							MPa	psi	
I	1A	0.358	0.445	7	CS	5/28	2.64	383	7
	1B				CS	5/28	2.45	353	7
	1C	0.358	0.445	7	L+CS	5/28	7.38	1070	7
	1D				L+CS	5/28	8.48	1230	7
	2A	0.358	0.445	21	CS	5/28	1.74	253	17
	2B				CS	5/28	2.64	383	17
	2C	0.358	0.448	21	L+CS	8/9	6.34	920	11
	2D				L+CS	8/9	6.20	900	11
	2E	0.358	0.300	21	CS	6/11	3.68	535	14
	2F				CS	6/11	3.44	500	14
	2G	0.358	0.342		CS	8/20	6.88	998	19
	2H				CS	8/20	8.69	1260	19
	3A	0.358	0.445	28	CS	8/9	5.14	745	30
	3B				CS	8/9	4.45	645	30
	3C	0.358	0.445	28	L+CS	8/9	6.43	933	28
	3D				L+CS	8/9	6.83	990	28
	3E	0.358	0.300	28	CS	6/11	4.03	585	31
	3F				CS	6/11	3.23	468	31
	3G	0.358	0.342	28	CS	8/20	6.74	978	34
	3H				CS	8/20	6.58	955	34
	4A	0.358	0.445	60	CS	11/22	5.35	776	64
	4B				CS	11/22	5.25	761	64

TABLE 34. (Cont'd)

Mix	Sample	Fly Ash/ as % of Total Solids	Water/ as % of Total Solids	Nominal Curing Time (days)	Test	Date Cast	Compressive Strength		Actual Age at (Test (days)
							MPa	psi	
	4C	0.358	0.445	60	L+CS	--	--	--	--
	4D				L+CS	11/22	6.55	950	60
	4E	0.358	0.300	60	CS	6/11	4.69	680	66
	4F				CS	6/11	4.34	630	66
	5G	0.358	0.342	45	CS	8/20	7.77	1127	46
	5H				CS	8/20	8.32	1207	46
II	1A	0.100	0.300	7	CS	6/16	9.69	1405	7
	1B				CS	6/16	9.14	1325	7
	1C	0.100	0.300	7	L+CS	6/17	16.20	2350	7
	1D				L+CS	6/17	14.65	2125	7
	2A	0.100	0.300	21	CS	6/17	6.89	1000	21
	2B				CS	6/17	6.12	888	21
	2C	0.100	0.300	21	L+CS	--	--	--	--
	2D				L+CS	--	--	--	--
	2E	0.100	0.445	21	CS	12/3	6.03	875	24
	2F				CS	12/3	7.55	1095	24
	3A	0.100	0.300	28	CS	6/17	8.65	1255	29
	3B				CS	6/17	10.00	1450	29
	3C	0.100	0.300	28	L+CS	12/3	14.71	2133	28
	3D				L+CS	12/3	15.24	2210	28
	3E	0.100	0.445	28	CS	12/3	6.33	918	28
	3F				CS	12/3	6.74	978	28

TABLE 34. (Cont'd)

Mix	Sample	Fly Ash/ as % of Total Solids	Water/ as % of Total Solids	Nominal Curing Time (days)	Test	Date Cast	Compressive Strength		Actual Age at Test (days)
							MPa	psi	
	4A	0.100	0.300	60	CS	6/16	10.89	1580	61
	4B				CS	6/16	10.98	1593	53
	4C	0.100	0.300	60	L+CS	6/16	13.79	2000	52
	4D				L+CS	6/16	12.98	1883	52
	4E	0.100	0.445	60	CS	12/3	7.44	1079	53
	4F				CS	--	--	--	--
III	1A	0.150	0.300	7	CS	11/8	9.48	1375	7
	1B				CS	11/8	8.57	1243	7
	1C				L+CS	--	--	--	--
	1D				L+CS	--	--	--	--
	1E	0.150	0.342	7	CS	1/6	10.24	1485	7
	1F				CS	1/6	10.47	1518	7
	2A	0.150	0.300	21	CS	10/21	11.38	1650	20
	2B				CS	10/21	11.00	1595	20
	2C				L+CS	11/8	14.65	2125	21
	2D				L+CS	11/8	14.38	2085	21
	3A	0.150	0.300	28	CS	10/21	11.46	1663	28
	3B				CS	10/21	13.53	1963	28
	3C				L+CS	--	--	--	--
	3D				L+CS	--	--	--	--
	4A	0.150	0.300	60	CS	--	--	--	--
	4B				CS	--	--	--	--

TABLE 34. (Cont'd)

Mix	Sample+	Fly Ash/ as % of Total Solids	Water/ as % of Total Solids	Nominal Curing Time (days)	Test	Date Cast	Compressive Strength MPa	Compressive Strength psi	Actual Age at Test (days)
	4C				L+CS	--	--	--	--
	4D				L+CS	--	--	--	--
	5A	0.15	0.300	14	CS	11/8	9.96	1445	14
	5B				CS	11/8	9.41	1365	14

NOTES: 1. CS = compressive strength
L+CS = specimen was leached as reported elsewhere and then checked for compressive strength.
2. "Age at test" means age at the end of the initial curing period, when the specimen was either tested for compressive strength or subjected to leaching.

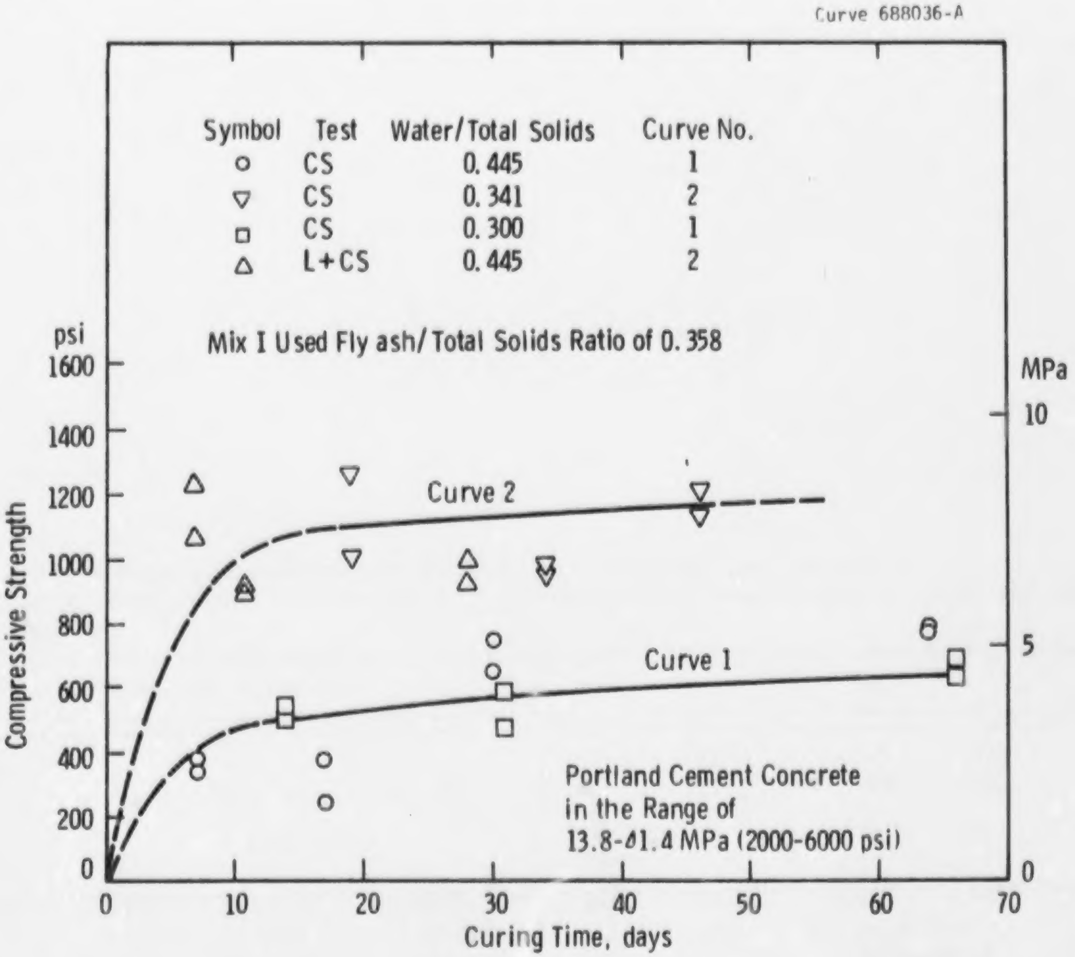

Figure 25. Compressive Strength of 5-cm Cubes Cast from Spent Solids from Exxon Run 27 Using Mix I

Curve 688035-A

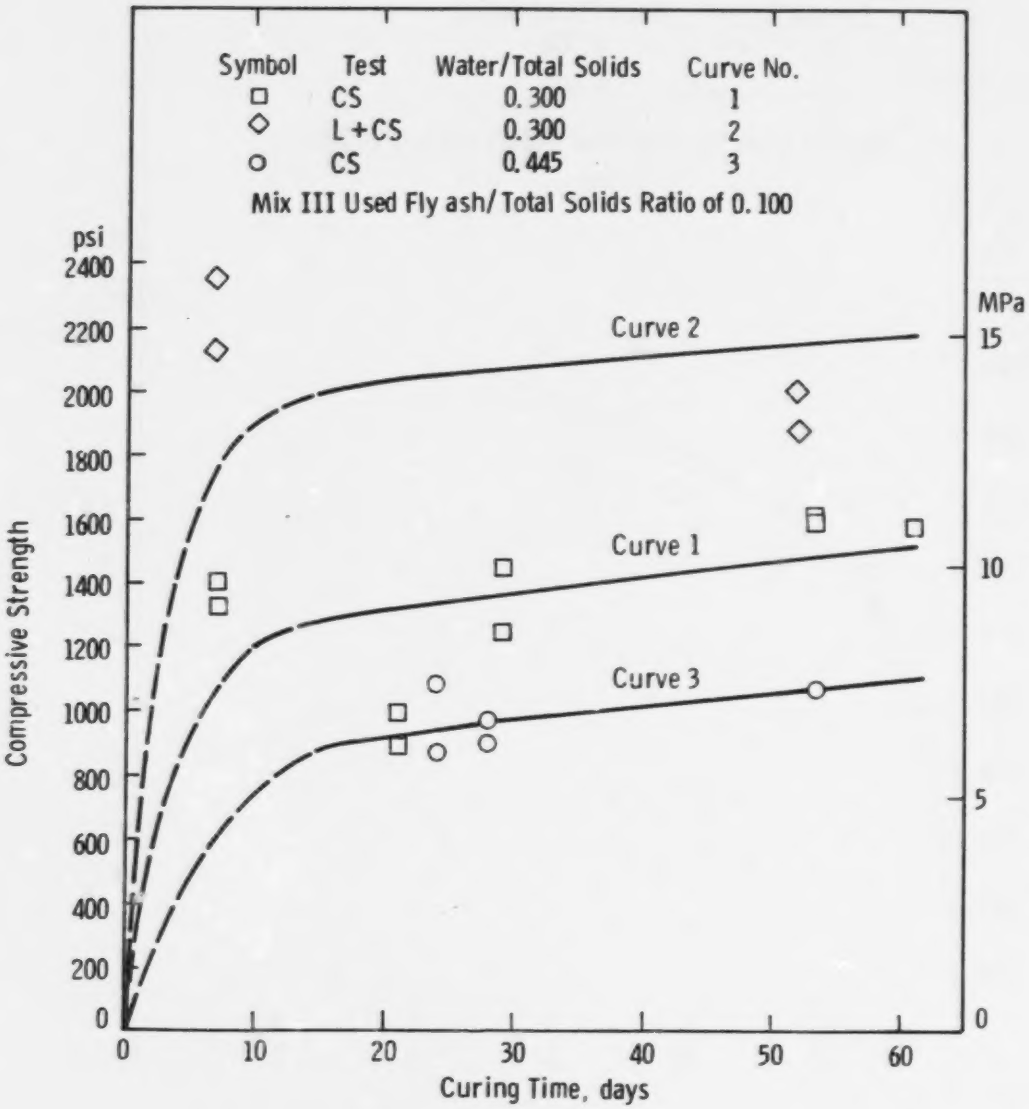

Figure 26. Compressive Strength of 5-cm Cubes Cast from Spent Solits from Exxon Run 27 using Mix II

Curve 688083-A

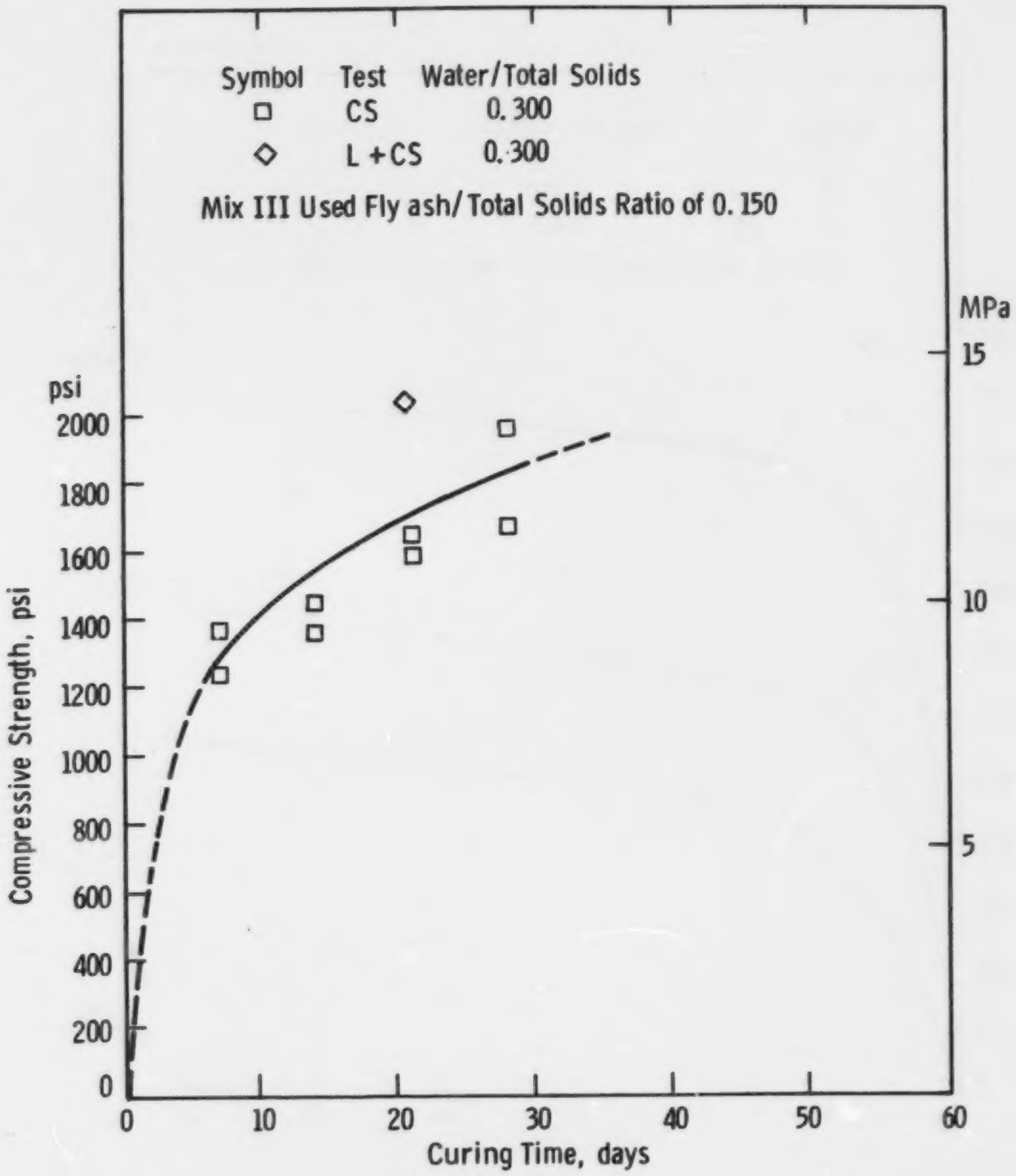

Figure 27. Compressive Strength of 5-cm Cubes Cast from Spent Solids from Exxon Run 27 Using Mix III

Curve 688082-A

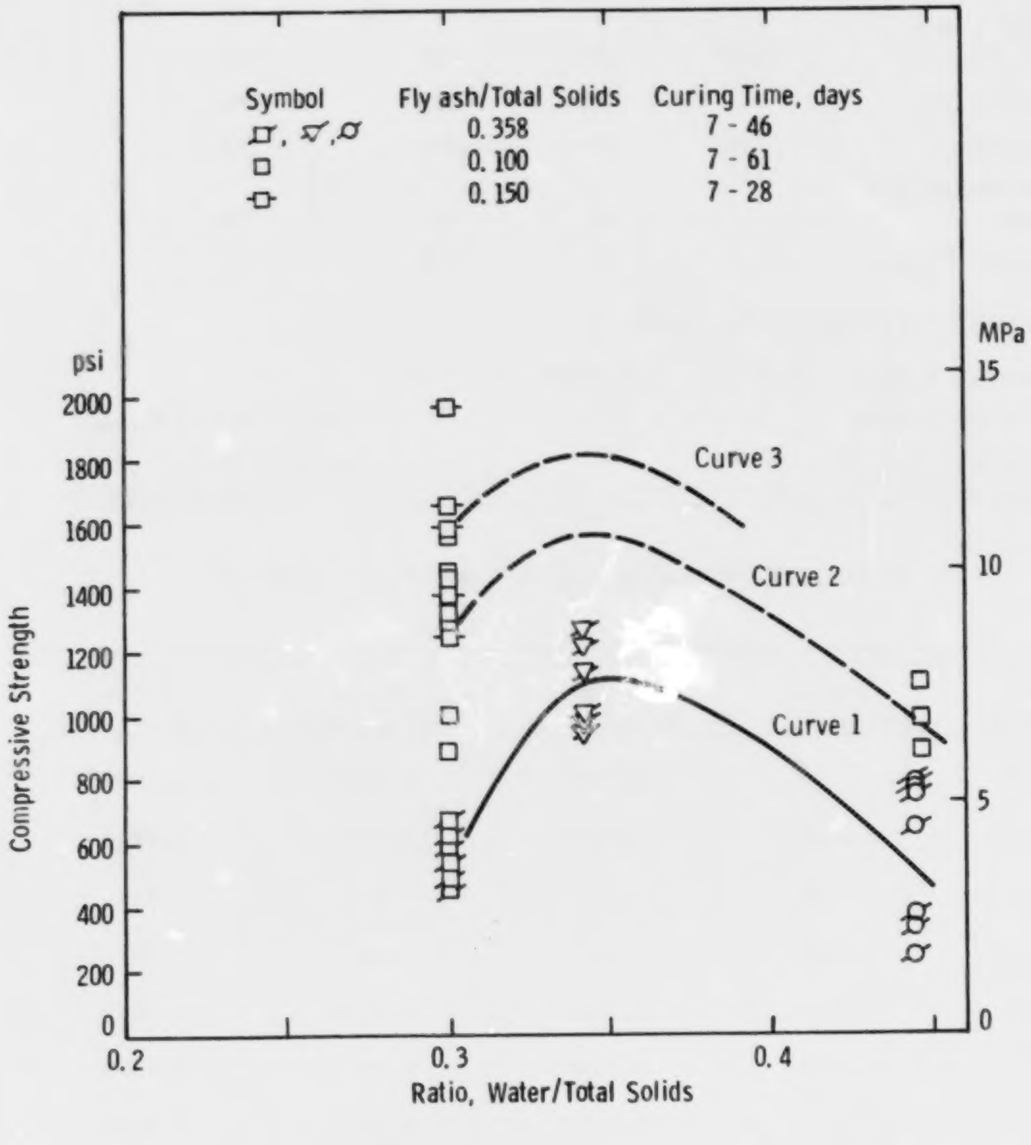

Figure 28. Effect of Water Content on Compressive Strength of 5-cm Cubes Cast from Spent Solids from Exxon Run 27

TABLE 35. COMPRESSIVE STRENGTH OF PER SPENT SORBENT MIXES

Composition (g)	PER-1	PER-2	PER-3	PER-4
PER spent sorbent	1000	600	250	600
CaO adder	--	300	500	300
Water	300	200	1000	500
Duquesne Fly Ash	--	--	--	100
Fused Silica	--	--	150	--
Compressive Strength, MPa (psi)				
Curing 4 days	0.034(5)	7.5(1090)	0.33(48)	
Curing 7 days	--	--	--	0.90, 0.83 (130,120)
Curing 17 days	--	--	--	1.07, 1.19 (155,173)

TABLE 36. ESTIMATED COMPOSITION OF PER COMPACTS

Basis	PER-1 moles/100g	PER-2 moles/1100g	PER-3 moles/900g	PER-4 moles/1000g
CaO(C)	-	4.5239	8.5718	3.7888
SiO_2(S)	0.4526	2.7156	3.6277	3.4628
Al_2O_3(A)	0.0121	--	--	--
Fe_2O_3(F)	0.0338	--	--	--
MgO(M)	0.0528	0.3168	0.1320	0.3416
C_3A	0.0885	0.6036	0.2515	0.7909
C_3F	--	0.2028	0.0845	0.2629
$CaSO_4$	0.2486	1.4916	0.6215	1.4916
Other	(6.31g)	(37.86g)	(15.775g)	(48.869g)

TABLE 37. COMPARISON OF COMPOSITION OF PER COMPACTS WITH NORMAL PORTLAND CEMENT

Composition	Portland Cement	PER-1	PER-2	PER-3	PER-4
CaO	69.22	28.44	63.41	68.80	57.45
SiO_2	27.57	51.96	26.57	27.92	30.67
Al_2O_3	3.21	19.60	10.02	3.28	11.88
	100.00	100.00	100.00	100.00	100.00

for the results obtained on PER-1/4. If constituents are allocated into compounds found in cement, in PER-1 the alumina content is in excess of that needed to tie up the unsulfated CaO as C_3A, or $(CaO)_3 \cdot Al_2O_3$. Hence, no CaO is available for SiO_2 or Fe_2O_3. Since the strength of normal cement is attributable largely to hydrated calcium silicates, the essentially zero strength of PER-1 is a reasonable expectation. Also, looking at the three main constituents of cement (CaO, Al_2O_3, and SiO_2), the as-is composition of the PER stone is definitely outside the Portland cement area.

PER-2 was intended to test a mix with the $CaO/(CaO + SiO_2 + Al_2O_3)$ ratio closer to 69.22 percent. This was accomplished by adding fresh lime to the residue. Although only 63.4 percent was achieved, the compact showed a substantial compressive strength (7.5 MPa or 1090 psi).

Since alumina in PER-2 was high, relative to that in Portland cement, mix PER-3 included both extra CaO and SiO_2. The extra silica was obtained by adding commercially available fused silica to the residue. Table 37 shows the composition achieved was very close to that of Portland cement, but apparently this was not sufficient since the compressive strength was very low (0.33 MPa or 48 psi). It may be that pulverized fused silica is not an effective pozzolan.

PER-4 used Duquesne fly ash from a conventional coal boiler as the silica source, limiting it to 10 percent of the total solids. The composition was appreciably lower in CaO and higher in Al_2O_3 than is normal cement. Compressive strength was somewhat higher than in PER-3, suggesting that silica in fly ash is a better pozzolan than ground fused silica.

A final conclusion on the free lime content needed was deferred, but the tests were considered to show PER stone must be ground.

ASSESSMENT OF UTILIZATION

Preliminary Flow Sheets

Figure 29 shows a schematic diagram of a flow sheet for spent sorbent collection from AFBC. Although industries such as iron and steel manufacture practice dumping hot slag, the FBC spent sorbent probably will have to be cooled as the minimum processing step. Since heat recovery of stack gas to combustion air may be utilized, except in large plants, as shown in a recent PER report,(31) the heat picked up from the spent sorbent will probably be discarded. Since contact with moisture will initiate pozzolanic reactions, the cooled material is sent to temporary enclosed storage and then sent via rail car to a processor. The flow sheet also shows secondary particulate removal, which might be a granular bed filter, to take full advantage of advanced technology.

From this flow sheet other possibilities can be derived. It may be economical to add on-site grinding facilities to reduce the spent sorbent to -125 mm or possibly -44 mm. The next stage would be to add facilities for making aggregate. Two variations are being examined, direct casting and isostatic pressing.

Preliminary Economics

In view of the rising cost of energy, attention was given to the possibility of a closer integration of basic industries. Table 38 shows figures for the energy consumption in the cement industry. Combining

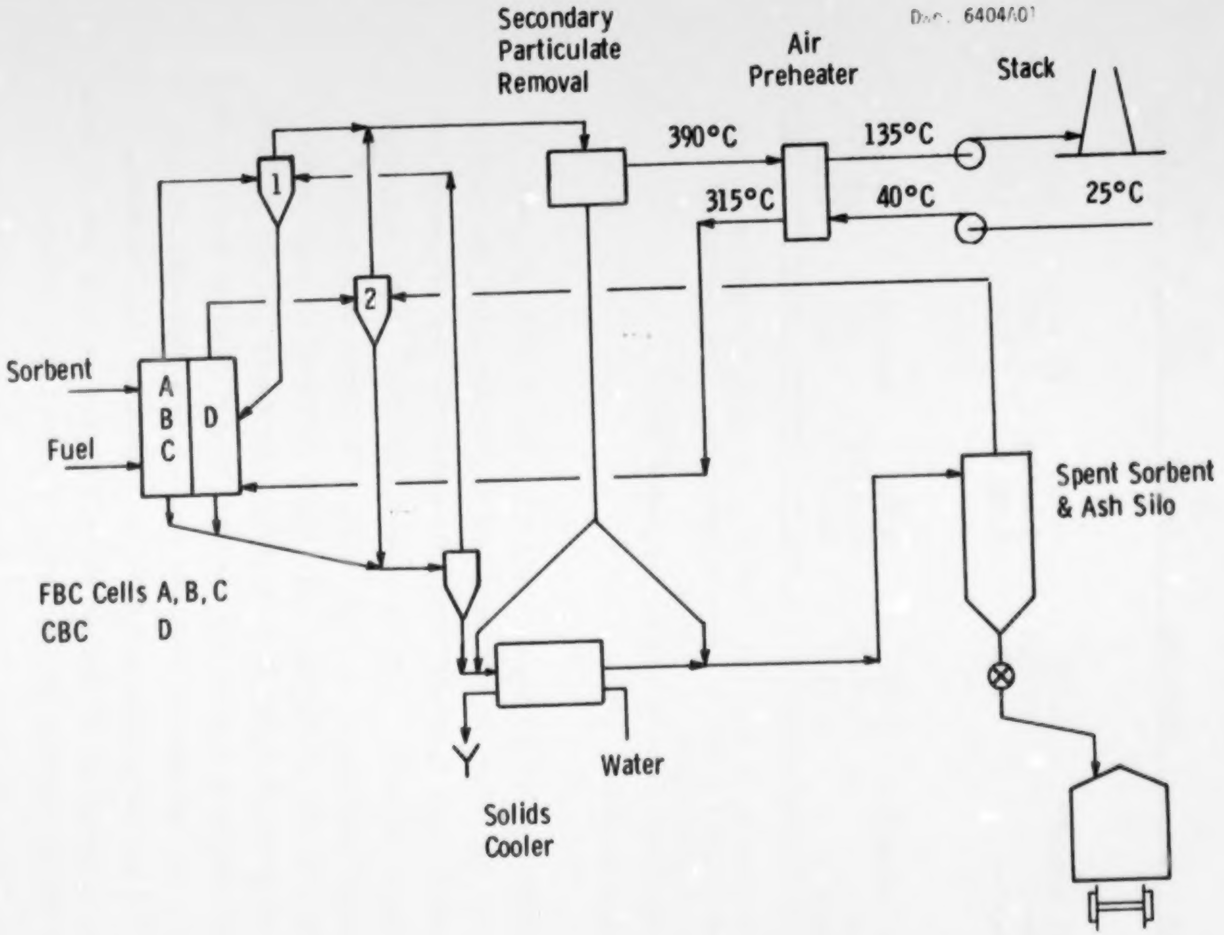
6404A01
Secondary
Particulate
Removal
Air
Preheater
Stack
390°C
135°C
315°C
40°C
25°C
1
2
Sorbent
Fuel
A
B
C
D
FBC Cells A, B, C
CBC D
Spent Sorbent
& Ash Silo
Water
Solids
Cooler

Figure 29. Spent Sorbent and Fly Ash Collection from Atmospheric-Pressure Fluidized-Bed Combustion

TABLE 38. ENERGY CONSUMPTION OF THE CEMENT INDUSTRY*

Process	Energy Source Coal, Mg	Oil (bbls)	Gas (CF)	Electricity (kWh)
Dry Processes				
Total annual usage**	3.599	0.775	62,484	3,948
Per bbl cement	0.02311	0.00499	402	25.42
Per ton cement	0.1229	0.0265	2140	135.2
Wet Processes				
Total annual usage**	5.036	4.987	140,436	5,621
Per bbl cement	0.02102	0.02082	586	23.46
Per ton cement	0.1118	0.1107	3118	124.8

*Unit quantities based on 155.337 x 10^6 bbl of cement produced by dry processes and 239.572 x 10^6 bbl by wet processes. One barrel of cement contains 376 pounds of cement.

**All total quantities in millions of indicated units.

Source: Minerals Yearbook, 1968

the different forms of energy input using 27 x 10^6 Btu/ton of coal, 6.3 x 10^6 Btu/bbl oil, 1000 Btu/CF gas, and 10,000 Btu/kWh; the energy requirement works out to 1,376,000 Btu/bbl cement for dry processes and 1,423,000 for wet processes. For comparison, the FEA(62) has estimated the average energy requirement at 1,391,000. The Conference Board(63) arrived at 1,318,000 for 1967, which has since declined through technological improvements to 1,218,000 in 1971. The Board did not include a breakdown, but the kiln itself may consume 700,000 Btu/bbl for the dry process, of which 95 percent is required for heating from ambient temperature to 900°C and calcining the $CaCO_3$ and $MgCO_3$ in the limestone. Additional heat is required to get to the clinkering temperature of about 2600°F, but is largely offset by exothermic clinkering reactions.

Two possibilities for integration with fluid-bed combustion arise. Close integration would feature transfer of the hot spent sorbent directly to a cement process. The Trief process(64) probably would be best suited to utilizing this approach, since the charge is fully melted rather than merely clinkered. Whether the dust problems of a cement plant are compatible with the air requirements of a large power plant needs careful review. Alternatively, the spent sorbent would be cooled and shipped to a cement plant at another location. There it would be ground to at least 74 μm and used as the CaO source. In this case, the saving in energy for the cement operation is only the calcination energy, which is about 54 percent of the kiln energy requirement. If applied to the entire production of 395×10^6 bbl of cement, the saving amounts to about 65,000 bbl of fuel oil equivalent (FOE)/day. This does not have tremendous national significance when compared to the daily demand of 17×10^6 bbl of petroleum in the United States or even to the heavy fuel oil demand of 2.4×10^6 bbl/day. Its importance is, therefore, indirect, since cutting the operating costs of cement manufacture would help keep down construction costs. At 378,000 Btu/bbl, fuel consumption would be reduced from 0.218 bbl FOE/bbl cement to 0.158, a reduction of 27 percent. With cement at $4.50/bbl and fuel oil at $10/bbl, the fuel cost represents half the cement price, and the saving is about 14 percent. Equally important factors may be the supply of limestone of a quality suitable for fluid-bed combustion and the economics of transportation.

Cement production requires about 0.21 Mg of limestone/bbl of cement or 33×10^6 Mg of limestone/year, which, by reference to the section in this report on market data, would correspond to the output of spent sorbent from about 48-1000 MWe FBC plants using limestone. The minimum-sized cement plant in 1971 appears to have produced about 1×10^6 bbl/year, with 16 percent producing over 5×10^6. A 3×10^6 bbl plant could take the output from a 1000 MWe power plant. Electrical requirement would be 76,000 MWh/yr or about 230 MW, based on a 330-day operating year. So an interesting possibility is for cement plants to generate their own electricity via an FBC plant. A larger plant could practice blending of the FBC spent sorbent with fresh limestone if there were technical reasons why the spent sorbent could not be used alone. A further projection is that, by 1980, 60 percent of the energy requirement of the cement industry will be coal, with another 8 percent from purchased electricity. In 1971, coal provided 35 percent and gas 45 percent of the energy requirement. Along with the higher consumption of coal is the higher production of coal ash, a potential source of pozzolan. A more detailed study of the profitability of the cement business is needed, however, to clarify the potential FBC market. The long-term growth rate has been about 2.8 percent/yr from 1909 to about 1967. Although this growth rate is expected to slow down, partly because imports will increase to 50 x 10^6 bbl/yr, there could be 100 x 10^6 bbl of domestic capacity required by 1980. Demand for hydraulic cement is expected to increase in this same period at the rate of 3.0 percent/year.

Analysis of Results

The work described in the foregoing sections has focused on determining the potential for utilizing FBC spent sorbent and associated fly ash. Simple tests have shown that stable, solid compacts can be produced by grinding the spent sorbent to -125 μm, combining it with coal fly ash, and adding water. Compressive strengths are adequate for landfill applications and may permit use of the mixes as replacement for concrete in low-strength fill applications. The initial work on isostatic pressing has revealed a potential for use in high-strength columns and in aggregate. Although a full demonstration of utilization is considered outside the scope of the present content, certain additional laboratory tests are under way to confirm further these potentials. Included are an examination of the Trief Process(61) under a related contract and of resistance to freeze-thaw conditions and to sulfate attack.

Process economics will be checked to identify any additional information that may be needed to support any recommended processing sequence.

From a broader view, the effect of requiring environmental protection is expected, in general, to increase the cost of power generation and probably the cost of most industrial operations. The pressure of increasing demand on finite resources is also strengthening the case for conservation. Power generation has grown as a separate entity in the economy from industrial production. Although plant expansion can certainly continue in the historical pattern, the work reported here has shown that potential exists for achieving both environmental protection and conservation by integrating power generation and cement production. Instead of each drawing upon high-quality limestone reserves, the limestone could be used first in a fluidized-bed combustor and then used to make either a new type of concrete or a new type of cement. Even if these new materials were found not to be as strong or as durable as those they might replace, these deviations might merely require modification of the design of the application.

SECTION 8

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APPENDIX A

THE FEASIBILITY OF OCEAN DUMPING AS AN INTERIM ALTERNATIVE TO DISPOSAL OF SPENT STONE FROM THE FLUIDIZED BED COMBUSTION PROCESS

20 September 1976

Report To: WESTINGHOUSE ELECTRIC CORPORATION
Research and Development Center
Churchill, Pennsylvania

By: J. M. Forns
WESTINGHOUSE OCEANIC DIVISION
Ocean Research Laboratory
Annapolis, Maryland 21404

INTRODUCTION

The oceans cover more than 70% of the earth's surface, incorporating approximately 140 million square miles with an average depth of more than 12,000 feet. They are critical in maintaining the world's environment, contributing to the oxygen-carbon dioxide balances in the atmosphere, affecting global climatology, and providing the base for the world's hydrologic system. Oceans are economically valuable to man in providing necessary food and mineral resources. In addition, they are a medium of transportation and recreation to more than 60% of the Nation's population. The continental margins of the world's oceans are the most important individual environmental areas from the standpoint of gross organic production. According to Odum (1959), estuaries and coastal oceans contribute more than 58% of the total primary caloric carbon energy for the entire planet. Any serious detrimental impacts on these marine systems could have far-reaching effects on our global environment in years ahead.

While our coastal oceans are biologically diverse, extending from tropical to arctic environments, they are also the ultimate receptacle for many of our wastes. Sewage, chemicals, construction debris, and many other waste materials are transported to the ocean by riverine systems or directly by barges, ships, and pipelines. Although the amount of waste presently dumped directly into the ocean is small compared to the total amount of wastes reaching the oceans, in the future the impact of ocean dumping, as a means of waste disposal, will increase significantly relative to that of other sources. Cognizant of this, the Council on Environmental Quality prepared in 1970 a formulation and recommendation for a national policy concerning ocean dumping. They concluded that the problem was growing rapidly and that in many cases, feasible and economic alternative methods were available for disposal of wastes currently being dumped at sea. They also realized that certain ocean dumping practices did not have immediate or viable alternatives and recognized that there was no regulatory authority controlling ocean dumping as the jurisdictions of individual State and the Army Corps of Engineers extended only within the three-mile territorial sea. Their report also pointed out the international implications of ocean dumping off the U.S. continental margins.

The purpose of the following report is to describe the present national position with regard to ocean dumping and identify the mechanisms and procedures of ocean disposal as it applies to the spent stone wastes from the fluidized bed combustion process. In no way is there any intention to predict future government policy concerning ocean dumping. The material in this report has been gathered and organized solely to present the established governmental criteria and evaluation process by which the federally designated ocean dumping permit system operates. The determination of ocean disposal feasibility is based on presently enacted legislation and existing precedents. Included in this report are specific sections dealing the the federal regulations, criteria and evaluation process, identification of approved sites for ocean disposal, the mechanisms to carry out an ocean dumping program, and the feasibility of dumping spent stone wastes at established ocean dumpsites.

FEDERAL REGULATIONS AND PERMIT PROCEDURES

Since 1970, two significant pieces of federal legislation have been enacted to establish a mechanism for evaluation and control of ocean dumping. The first passed in 1972, is known as the Marine Protection, Research and Sanctuaries Act (MPRSA) (Appendix A). This pulblic law (92-532) enables Congress to establish a national policy on ocean dumping and to regulate the dumping of all types of materials into the oceans. It also establishes a system to prevent or strictly limit the ocean disposal of any materials which would adversely affect human health and the marine environment, ecological systems, or economic potentialities. This Act became effective April 23, 1973, and since that time, all ocean dumping of waste materials has been done under a permit from EPA, except for dredged spoils which are regulated by the Corps of Engineers.

When the ocean dumping program was first initiated, many procedural and technical decisions were encountered resulting in the development by EPA of Final Regulations and Criteria (Appendix B) to be included in the MPRSA. These Final Regulations governing ocean dumping were published in the Federal Register, October 15, 1973, and constitute the legal requirements which must be followed by anyone using the oceans for waste disposal. The combination of Title I of the MPRSA and the Final Regulations put out by EPA establish a permit granting procedure to utilize designated ocean dumpsites for five categories including industrial wastes, sewage sludge, construction and demolition debris, solid wastes, and explosives. Presently, of the total 281 available disposal areas, eleven ocean dumping sites in the Atlantic Ocean and Gulf of Mexico are now in active use for disposal of municipal and industrial wastes. There is no dumping of these wastes in the Pacific Ocean, although sewage sludge is currently being discharged via several outfalls.

Since the legislation was established ocean dumping activity showed a net increase of about 1.6 million tons from 1973 to 1974, primarily because of a 1.1 million ton increase in construction and demolition debris. While figures are not yet available, EPA expected to reduce this volume somewhat because alternative methods of disposal are being developed and implemented. According to EPA (1975), the major problem in the future with regard to ocean dumping is the anticipation of increased pressures to dispose of wastes at sea resulting from more and better waste treatment facilities removing increased amounts of wastes from both municipal and industrial sources. Clearly, the understanding and technology required to deal with waste disposal has not kept pace with population growth. EPA's basic approach has been to find and use the least environmentally damaging site and methodology of waste disposal whether it be via air, land, or water.

The basis for regulation of ocean dumping is given in the form of criteria which reguire EPA to balance several factors before determining whether or not to issue a dumping permit. These factors, which are the essence of the federal regulation on ocean dumping, include:

1. The need for the proposed dumping in the ocean, as determined by EPA.
2. The effect of dumping on the marine environment.
3. Social and economic considerations involving the dumping, including effects on human health and welfare, fishery, and recreational resources.
4. Alternative means of disposal, including alternate methods of treatment, land-based disposal and recycling.
5. The feasibility of dumping beyond the continental shelf.

Upon consideration of these factors, EPA, through the regional offices, will consider application for a permit for ocean dumping. Schematically, Figures 1 and 2 show the procedural sequence in obtaining dumping permits. In Figure 1 the procedure covers the application process where waste disposal takes place within a single EPA region's jurisdiction. Figure 2 describes the application procedure for inter-regional permits.

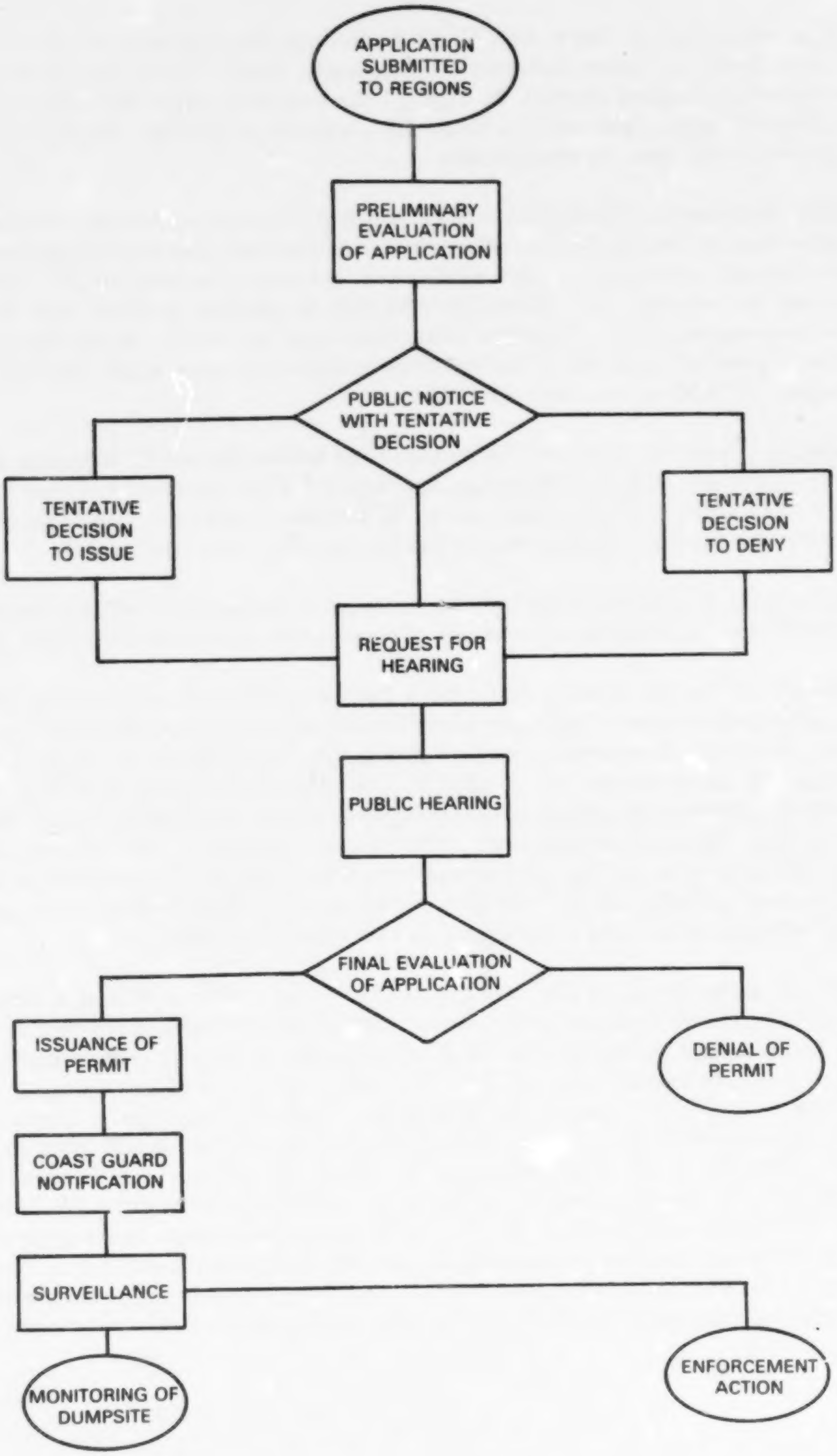
One important aspect of the Federal Regulations and Criteria is contained in Section 220.3 (d) (2). This specifies that an "interim permit will reguire the development and active implementation of a plan to either eliminate...or bring it within limitations of...the ocean dumping criteria". While interim permits may not be renewed, new interim permits may be granted provided that the permitee completes the sequence of phases required to meet ocean dumping criteria. By this mechanism EPA intends to limit the use of ocean dumpsites wherever possible and allow ocean disposal only when materials dumped fall within the criteria identified.

On Monday, June 28, 1976 EPA published in the federal register a "Proposed Revision of Regulations and Criteria" on Ocean Dumping (Appendix C). These proposed revisions, if and when promulgated, would affect both the procedures to be followed in reviewing applications for ocean dumping and the substantive criteria to be applied in evaluating those applications.

Several aspects of these revisions would directly affect the feasibility of the disposal of spent stone by ocean dumping. Following is summary of those salient aspects of the proposed revisions.

Section 102 of the Act requires that criteria for the issuance of ocean disposal permits be promulgated after consideration of the environmental effect of the proposed dumping operation, the need for ocean dumping, alternatives to ocean dumping, and the effect of the proposed action on esthetic, recreational and economic values and on other uses of the ocean. Parts 227, 228 of the proposed revisions constitute the criteria established pursuant to Section 102 of the Act. The decision of the Administrator, Regional Administrator or the District Engineer, to issue or deny a permit and to impose specific conditions on any permit issued with be based on an evaluation of the permit application pursuant to these criteria. Following is a summary of those criteria which apply to the ocean disposal of spent stone from the fluidized bed combustion process.

Section 227 states that if an applicant can satisfy the following conditions, a permit will be granted. First, the applicant must satisfy the environmental impact criteria of sub-part B. Several of these criteria apply to spent stone. Section 227.7 (d) states that in the dumping of wastes of highly acidic or alkaline nature consideration shall be given to: 1) the effects of any change in acidity or alkalinity of the water at the disposal site; and 2) the potential for synergistic effects or for the formation of toxic compounds at or near the disposal site. It further states that allowance may be made in the permit conditions for the capability of ocean waters to neutralize acid or alkaline wastes; provided, however, the dumping conditions must be such that the average total alkalinity or total acidity of the ocean water after allowance for initial mixing, may be changed, based on stoichiometric calculations, by no more than 10 percent during all dumping operations at a site. A definition of initial mixing is given in Section 227.29 of subpart as that dispersion or diffusion of a waste which occurs within four hours after dumping. In addition, several methods are listed which can be used to estimate this.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PRELIMINARY EVALUATION OF APPLICATION
PUBLIC NOTICE WITH TENTATIVE DECISION
TENTATIVE DECISION TO ISSUE
TENTATIVE DECISION TO DENY
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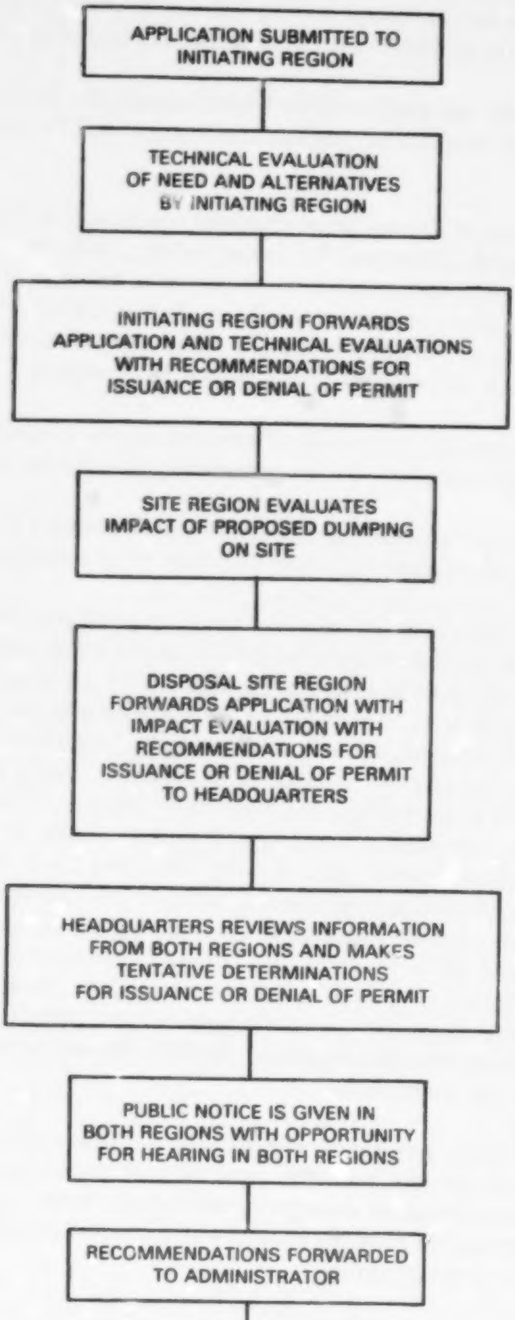
PUBLIC HEARING
FINAL EVALUATION OF APPLICATION
ISSUANCE OF PERMIT
DENIAL OF PERMIT
COAST GUARD NOTIFICATION
SURVEILLANCE
ENFORCEMENT ACTION
MONITORING OF DUMPSITE

Figure 1. EPA Regional Permit Application Procedure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SITE REGION EVALUATES IMPACT OF PROPOSED DUMPING ON SITE
DISPOSAL SITE REGION FORWARDS APPLICATION WITH IMPACT EVALUATION WITH RECOMMENDATIONS FOR ISSUANCE OR DENIAL OF PERMIT TO HEADQUARTERS
HEADQUARTERS REVIEWS INFORMATION FROM BOTH REGIONS AND MAKES TENTATIVE DETERMINATIONS FOR ISSUANCE OR DENIAL OF PERMIT
PUBLIC NOTICE IS GIVEN IN BOTH REGIONS WITH OPPORTUNITY FOR HEARING IN BOTH REGIONS
RECOMMENDATIONS FORWARDED TO ADMINISTRATOR
FINAL ACTION BY ADMINISTRATOR

Figure 2. Permit Procedure for Interregional Application for Ocean Dumping

Section 227.7 (c) states that wastes containing biodegradable constituents, or constituents which consume oxygen in any fashion, may be dumped in the ocean only under conditions in which the dissolved oxygen after allowance for initial mixing will not be depressed by more than 25 percent below the normally anticipated ambient conditions in the disposal area at the time of dumping.

Section 227.8 states that no wastes will be deemed acceptable for dumping unless they can be dumped so as not to exceed the "limiting permissible concentrations." This is defined in Section 227.27 as:

> 1) "that concentration of a material or chemical constituent in the receiving water which, after reasonable allowance for initial mixing, will not exceed a toxicity threshold defined as 0.01 of a concentration shown to be toxic to appropriate sensititve marine organisms in a bioassay carried out in accordance with approved EPA procedures; or 2) 0.01 of a concentration of a waste material or chemical constituent otherwise shown to be detrimental to the marine environment."

In section 227.27 (b) a definition of "appropriate sensitive marine organisms", and the necessary experimental conditions and procedures for an acceptable bioassay are given.

Section 227.9 states that the quantity of the substance dumped at any single time and place must be controlled to prevent damage to the environment or to amenities.

After satisfying the environmental impact criteria, the applicant must secondly demonstrate a need for ocean dumping. The specific detailed factors which will be considered in determining if there is a need for ocean disposal of a material are given in subpart C (sections 227.14 - 227.16). The degree of treatment feasible for the waste and to what extent this will be carried out will be considered. The process by which the waste is generated will be examined to see if this process is essential to the provision of the applicants goods or services or to see if less polluting materials could be used. A consideration will be made of the relative environmental impact and cost for ocean dumping as opposed to other feasible alternatives including, but not limited to: land fill; well injection; incineration; spread of material over open ground; recycling of material for reuse; additional biological, chemical or physical treatment of intermediate or final waste streams; and storage. At the same time, a consideration of any irreversible or irretrievable consequences of the use of the alternatives to ocean disposal will be made. It must be determined after these considerations that there are no practicable alternative locations and methods of disposal (i.e., which are available at reasonable incremental cost and energy expenditures, which need not be competitive with the costs of ocean dumping, taking into account the environmental benefits derived from such activity) or recycling available which would be less detrimental.

In addition, the administrator may, at his discretion, grant the permit with other terms and conditions. He may require that the permittee terminate all ocean dumping by a specified date, or continue research and development of alternative methods of disposal and make periodic reports of such research and development in order to provide additional information for periodic review of the need for an alternative to ocean dumping.

The third major requirement is that there can be no unacceptable adverse effects on esthetic, recreational, or economic values of the ocean. The criteria used for making a judgement of this are given in subpart D (section 227.17 - 227.19).

In section 227.18 it is stated that the following factors will be considered in making a determination of this impact: present recreational and commercial use of areas which might be affected by the proposed dumping; existing water quality and disposal activities in the areas which might be affected: applicable water quality standards; visible characteristics of the materials which result in an unacceptable esthetic nuisance in recreational areas; presence in material of toxic chemical substances released in volumes which might affect humans directly; bioaccumulative or persistent chemical constituents which may affect humans adversely directly or through food chain interractions; and constituents in the material which might significantly affect living marine resources of recreational or commercial value.

A fourth condition upon which being granted a dumping permit is contingent is that the proposed dumping will not have an unacceptable adverse effect on "other uses" of the ocean. These uses, listed in section 227.21 of subpart E, are as follows: commercial and recreational fishing; commercial and recreational navigation; actual or anticipated exploitation of living marine resources as well as non-living resources such as mineral deposits, oil and gas exploration and development, future offshore marine terminal or other structure development; and possible scientific research and study. The assessment of impact on other uses of the ocean will consider both temporary and long-range effects within the state-of-the-art, but particular emphasis will be placed on any irreversible or irretrievable commitment of resources that would result from the proposed dumping.

If, in fact, all the criteria presented under the above four broad headings are satisfied, a permit for ocean disposal can be issued.

Permits are of different kinds. Section 220.3 liss them and describes each. A "general permit" may be issued for dumping certain materials which will have minimal adverse environmental impact and are generally disposed of in small quantities, or for specific classes of materials that must be disposed of in emergency situations. They may be issued with or without application whenever the Administrator determines that is is necessary or appropriate.

A second kind of permit is a "special permit" which may be issued for materials which satisfy those criteria discussed above. They are issued with an expiration date no later than three years from the date of issue.

A third kind of permit, an "interim permit" is described in section 220.3 as one which may be issued under certain conditions in accordance with subpart A of part 227 to dump materials which are not in compliance with the environmental impact criteria of subpart B of part 227, or subparts D or E or for which an ocean disposal site has not been designated on other than an interim basis. Subpart A says essentially that interim permits will be granted when it is determined that even though all the criteria are not satisfied, the need for dumping and unavailability of alternatives are of greater significance to public interest than the potential for adverse effects on any aspect of the ocean. An interim permit is not valid for more than one year and requires substantial efforts by the permit recipient to bring the waste within the limitations required of a special permit or to take the necessary measures to cease ocean dumping. A limitation, though, found in the description of interim permits in section 220.3 may make an interim permit unattainable for spent stone. It states that no interim permit will be granted for the dumping of waste from a facility which has not previously dumped wastes in the ocean, from a new facility, or from the expansion or modification of an existing facility, after the effective date of these regulations.

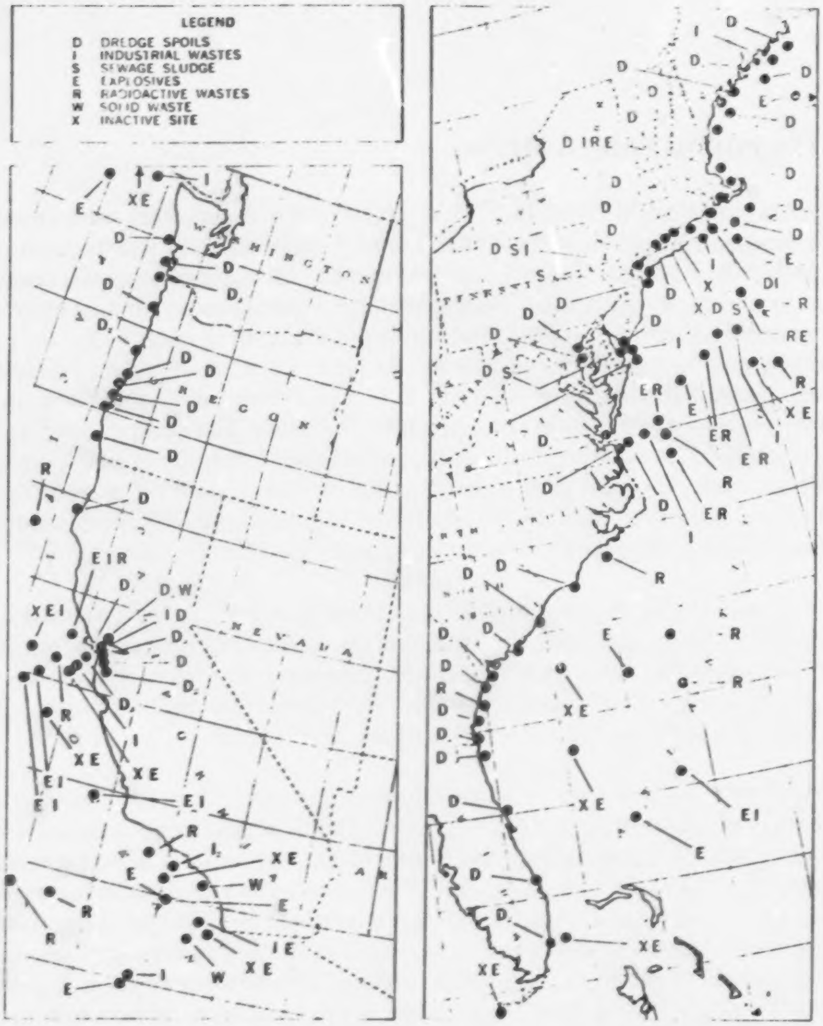
Part 228 is an altogether new addition to the existing regulations with no counterpart in them. It serves to establish the criteria for the management of ocean disposal sites by EPA, and presents criteria for the selection of sites, and factors which must be considered with respect to the determination of the permissible levels of disposal of materials at a particular site. It states the belief that permit issuance should not be based solely on the testing of waste, but that the specific marine environment must be considered. In addition, limitations are placed on the times and rates of disposal of materials (sec. 228.7) and an appropriate monitoring program is made (228.9). It is stated in this section that EPA will require the full participation of the permittee in the development and implementation of the monitoring program. Section 228.12 lists sites which will, beginning on the effective date of these regulations, be approved for dumping certain materials therein indicated on an interim basis pending completion of baseline or trend assessment surveys and designation for continuing use or termination of use.

APPROVED SITES FOR OCEAN DUMPING.

Prior to the enactment of MPRSA in 1973, a total of 281 disposal areas were known to exist within the estuaries and coastal oceans of the United States. Figure 3 shows these disposal sites in the Atlantic, Pacific, and Gulf of Mexico. From Table 1 more than half the ocean disposal sites were used by the Army Corps for dredge spoil disposal. The second largest use of ocean dumping by location was for industrial wastes constituting 13.7% of the total number of dumpsites available. It is the location of these dumpsites that is of concern when considering the spent stone wastes from the fluidized bed combustion process. These industrial disposal areas are located between 15 and 100 miles offshore depending on the type of waste and established regulatory procedure. For example, acid wastes from the New York metropolitan area are dumped in a designated zone 15 miles from New York City while certain chemically toxic materials must be disposed of at distances more than 125 miles offshore. Most of the industrial disposal in the Gulf of Mexico is conducted beyond the 400-fathom contour, which in the case of Galveston, Texas, requires a transport of more than 125 miles one way.

By contrast sewage sludge disposal sites account for a mere 0.6% of the approved dumpsites and are all within 50 miles of shore. However, when comparing the total tonnage (Table 2) of ocean dumped municipal and industrial wastes, sewage sludge comprises greater than 50% of the amount of waste disposed at sea. It is interesting to note that these wastes do not meet the criteria identified in the Final Regulations and yet additional interim permits have been issued.

It is important to note that only 11 of the 42 municipal and industrial dumpsites from the Atlantic and Gulf regions are considered active by EPA. This is primarily because most industrial dumpers have found alternatives to ocean dumping or the costs of disposal and subsequent monitoring have become uneconomic. While the remaining 31 sites are presently on the inactive list, they could be utilized once again. For such a case, it would have to be determined by EPA that the proposed ocean dumping constitutes the least deleterious environmental impact, does not infringe on other socio-economic potentials and the wastes to be dispossed have no other feasible alternative. If, however, the wastes meet the criteria specified in the Final Regulations, then an interim permit could be given which would be subject to review before continuance. The review cycle is presently on an annual basis. At each review the permitee would have to state the plan and phases for alternatives to ocean disposal, show the results of monitoring effects and provide quantitative environmental information to substantiate the case for ocean dumping.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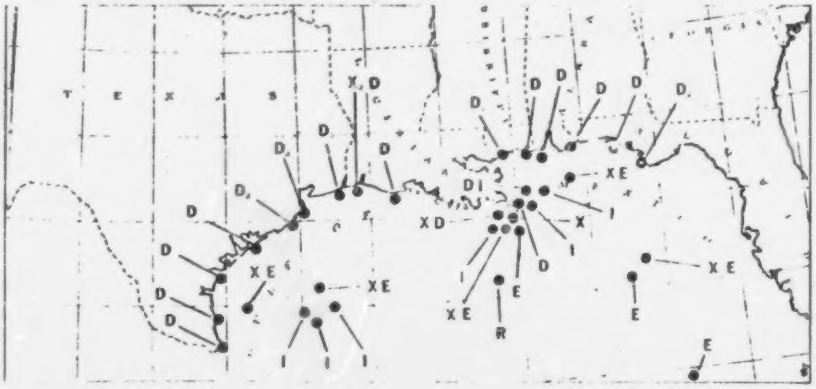

Gulf

Figure 3. Ocean Disposal Areas Along the U.S. Continental Margins

Table 1. Ocean Waste Disposal Areas (By Region and Waste Type)*

	DISPOSAL AREAS			
WASTE TYPE	PACIFIC	ATLANTIC	GULF	TOTAL
Dredge spoil	15	83**	63	161
Industrial waste	9**	15**	16	40
Sewage sludge***	0	2	0	2
Refuse	3**	0	0	3
Radioactive waste	10**	25**	2	37
Explosive and chemical ammunition	19**	19**	11	49
TOTAL (no duplicates)	54	135	92	281

* Revised and updated by James L. Verber, Food and Drug Administration, U.S. Department of Health, Education, and Welfare.

** Areas used for two or more types of wastes.

*** Does not include outfalls

Table 2. Ocean Disposal: Types and Amounts, 1974* and 1973**
(In Tons, Approx.)

WASTE TYPE	ATLANTIC		GULF		PACIFIC		TOTAL	
	1974	1973	1974	1973	1974	1973	1974	1973
Industrial Waste	4,767,000	3,997,100	950,000	1,408,000	0	0	5,717,000	5,405,100
Sewage Sludge	5,676,000	5,429,400	0	0	0	0	5,676,000	5,429,400
Construction & Demolition Debris	2,242,000	1,161,000	0	0	0	0	2,242,000	1,161,000
Solid Waste	0	0	0	0	200	240	200	240
Explosives	0	0	0	0	0	0	0	0
TOTAL	12,685,000	10,587,500	950,000	1,408,000	200	240	13,635,200	11,995,740

*1974 Source – EPA Regional Offices. Unpublished Reports, updated information, 1974 (12 months of dumping activity).

**1973 Source – EPA Regional Offices. Unpublished Reports, 1973 (8 months of dumping activity – May to December 1973 under permits issued by Ocean Disposal Program extrapolated for 12 months to provide an annual rate).

OCEAN DUMPING MECHANISMS

Proceeding with an ocean dumping program requires the establishment of specific ground rules before planning, organization, estimating, and governmental regulatory permits can be given. For spent stone wastes from the fluidized bed combustion process, several initial assumptions must be made including:

1. Materials will be of sufficient quantity to utilize a standard dumping vessel operating on a semi-regular schedule.
2. For initial evaluations, the spent stone will be taken unprocessed, directly from the combustion apparatus in a dry granular form.
3. Disposal will be at established ocean dumpsites designated for industrial wastes.
4. Transport will be from major seaport locations on the Atlantic and Gulf costs by a commercially established dumping operator.

The vessel type for disposal of granular spent stone will be determined by the magnitude of initial dispersion desired, ultimate physical fate of the waste and the relative economic advantage. As this material falls into the category of dry solid waste, similar to crushed rock or constructive debris, the most probable vessel type to be used is the deck barge with over-the-side dumping. Perhaps the more modern barges with clamshell bottoms can be used. Deck barges are most frequently used because disposal time is relatively long. This allows for spreading of the disposed materials over a large area and minimizes concentrated buildup in a small area of the dumpsite. For spent stone disposal, deck barge dumping can be accomplished by hydraulic jets flushing the material overboard or by changing mass to tip down one side of the barge to allow gravity dumping. While dilution and dispersion over large areas is desirable for liquid wastes, controlled concentration and even spreading is desired for particulate wastes.

Various types and sizes of dumping craft are used for specific operations. The deck barges which would be used for spent stone dumping employ different dump actuating mechanisms. It is these differences which determine the physical characteristics of ocean dumped materials. Older type vessels have six to eight pockets, each equipped with double gravity dump doors on the bottom. Others have a hinge type configuration consisting of port and starboard sections hinged topside fore and aft. Large hydraulically-operated pistons beneath the hinged doors allow controlled gravity forced release of the materials dumped. Most modern barges are remotely operate from the towing vessel which is equipped with Loran navigational aid for positive positioning when locating the dumpsite.

Several physical factors influence the disposal of dumped material from the barges. The same parameters used to control the physical characteristics and effects of disposed material are the principal considerations affecting the cost of ocean dumping. Included are such conditions as discharge rate, water depth, barge capacity, distance to the disposal site and chemical reactivity of the dumped materials. Based on existing practices, barging economics have been calculated by EPA (1971). From their data, bulk industrial wastes which include spent stone, would in 1971 cost approximately \$1.00 in the Pacific, \$1.80 in the Atlantic and \$2.30 along the Gulf Coast for each ton of material dumped. The principal reason for these costs is the need to travel great distances to reach deep waters where industrial dumpsites are located. Deep waters can be reached within 20 miles from shore along the west coast, but one way distances along the eastern Atlantic and Gulf coasts are as much as 100 miles from shore. From Figure 4, 5, and 6 by EPA (1971) one gets a rough order estimate of the dumping costs for ocean disposal of industrial waster such as spent stone from the fluidized bed process.

Although ocean dumping has been declining in total tonnage in the past two years, primarily because of the EPA permit system, there are many dumping operators along the Gulf and Atlantic coasts. In 1975 EPA reported that 11 private companies were involved in industrial waste ocean disposal operating under the regulations provided in the permit system. Table 3 includes most of these operators and their present bases of operation. The primary reason for the observed decline in ocean dumping has been the reluctance of EPA to issue permits, especially in cases where the wastes to be disposed do not meet the criteria set forth in the Final Regulations. As a result, many operations which previously went unchallenged are now being scrutinized by the permit process. More industrial waste disposers are finding alternative methods to disposal at sea or recycling wastes. However, since the basic premise of MPRSA and the Final Regulations is to seek out the least environmentally damaging means of waste disposal, the oceans will undoubtedly continue to be used as a receptacle for man's waste.

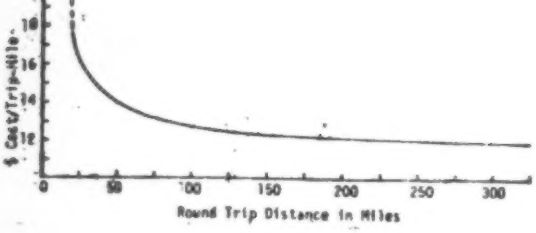

Figure 4. Cost Per Trip Mile as a Function of Round Trip Haul Distance

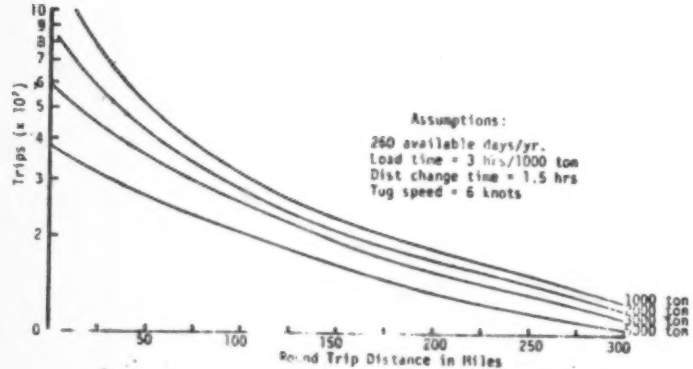

Figure 5. Limiting Number of Trips Per Year For Preset Barge Sizes

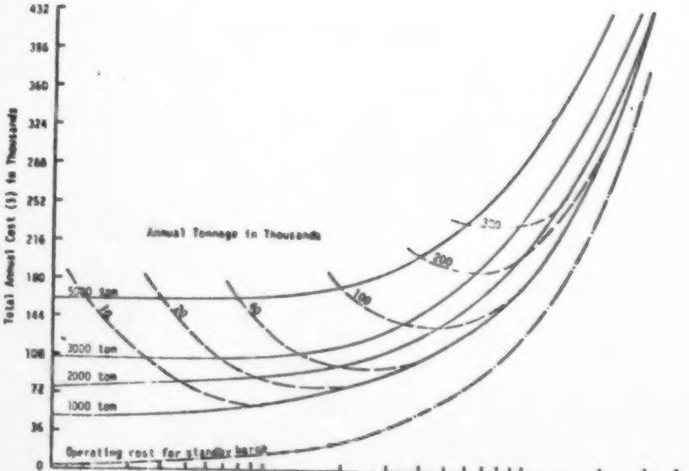

Figure 6. Annual Operating Costs for Round Trip Haul Distance of 100 Miles

Table 3. Ocean Dumping Operators Licensed by EPA

EPA Approved Ocean Dumpsites	Departure Points	Number of Operational Barges
Safety Projects & Eng. Co.	Hingham, Mass.	1
Pine State By-Products	Portland, Me.	1
A & S Trans. Co.	S. Kearny, N.J.	2
Spentonbush Trans. Service	NYC, N. Y.	3
Sun Trans. Co.	Marcus Hook, Pa.	1
Interstate Ocean Disposal Trans. Co.	Marcus Hook, Pa.	1
Port Arthur Towing Co.	Beaumont, Tx. La Porte, Tx.	4
DuPont Lessee	Beaumont, Tx. La Porte, Tx.	1
Domar Ocean Trans. Ltd.	Beaumont, Tx. La Porte, Tx.	6
Dixie Carriers Inc.	Deer Park, Tx.	2
Lockport Chemical Co.	Baton Rouge, La.	1

FEASIBILITY OF DUMPING SPENT STONE AT SEA

There are two philosophies regarding the dumping of wastes at sea. In the first case, certain ocean areas which are deemed to have limited ecological and sociological significance are designated for waste disposal. Dumping is conducted in such a way that any adverse biological effects are restricted to the dumpsite; the area is "written off" and hopefully the surrounding environment not affected. Generally this philosophy is used to regulate ocean diposal activities in areas off the continental shelf in deep waters. This rationale of waste disposal has been adopted for most industrial wastes.

The second philosophy regarding waste disposal in the ocean establishes a classification system of entire ocean environments within range of the generated wastes. This categorization of the marine environment is based on the potential or present used of the various areas, taking into consideration such sociological and ecological values as prime fishing areas, recreational zones or spawning areas. For each of these designated environments acceptable types and concentrations of wastes can be computed and dumping proceeds until the area has reached the saturation point for the particular waste. Upon reaching these specified concentrations dumping must cease until the ecology can absorb the waste and thereby lower the pollutant concentration. This attitude points toward dispersed dumping in shallow or surface waters. While segregating wastes to restrict the dumping of particularly toxic or nondegrading materials in these areas, this philosophy of ocean disposal often finds conflicts between sociological and ecological values. It would not be suitable for the consideration of industrial wastes.

Considering ocean dumping of the spent stone from the fluidized bed combustion process, the first philosophy may be acceptable if controlled disposal at designated sites is demonstrated to have a minimal impact. As a result, most locations for spent stone disposal would be at offshore areas as much as 100 miles from the nearest point of embarkment. The feasibility of using the oceans for waste disposal under the established permit system requires that certain measures be taken. The material to be disposed must be characterized. Quantities must be estimated. Physical characteristics as well as chemical constituents must be identified for conditions in a natural state and as the result of seawater mixing. Such particulars as elemental composition, reactive state, and particulate sizes of the material must be quantitated. This characterization must then be checked against the evaluation criteria set forth in the Final Regulations and any amendments to the regulations. Biological impact assessment must be performed.

The Westinghouse Ocean Research laboratory has performed some initial impact assessments of the spent stone likely to the generated from the fluidized bed combustion process. A preliminary feasibility evaluation was performed with CAFB stone in various mixtures of seawater taken off the coast of Maryland in the vicinity of two existing mid-Atlantic dumpsites. The area from which the seawater was taken represents two sites which EPA Region III has issued dumping permits for municipal sewage wastes and industrical liquid wastes (acids with an average pH of 0.1). The initial tests performed included CAFB stone/seawater mixing experiments to identify solution characteristics, heat release and chemical changes. Using sample material provided by the Westinghouse R&D Center, a series of scale experiments were undertaken. Calculations for these experiments were based on an average barge capacity of 2,600 cubic yards, average barge area of 15, 922 ft.^{2}, a measured density of 1.294 gm/cm^3 for the CAFB stone and at least 1,200 ft. depth where dumping would take place (just off the continental shelf). Scaling this down we were able to work with a thoroughly mixed spent stone concentration of 4.7×10^3 mg/l.

The first test undertaken was a simple mixing evaluation to determine the proportions of material which actually settled out. A series of 50 gram aliquots of CAFB stone were mixed in 1 liter settling tubes with seawater for 1 and 2 minutes and allowed to settle for 1, 3 and 18 hours. Data for this test are given in Table 4. Two distinct liquid phases were observed, a surfactant layer and a lower flocculant layer. The surfactant layer was a soapy, thinnly clouded mixture while the flocculant was a more dense wooly mixture. From the results in Table 4, 7 to 30% of the CAFB stone remained suspended in the water column over the 18 hour test. As expected, the surfactant layer comprised a greater percentage of the water column with time and the concentration of suspended particulates (greater than 0.45μ) decreased from 340 to about 12 mg/l. The lower flocculant layer comprised a smaller percentage of the water column, but its concentration increased from 2.8×10^1 mg/l to 1.6×10^2 mg/l. It is interesting to note that there is not an equilibrium effect where the total suspended solids remain the same and their proportions in each layer shift. It appeared that the flocculant layer near the bottom continued to react with the seawater and particulate material was released throughout the entire 18 hours. As a result, a continuous dense layer remained just above the sediment mound. Comparing this test with actual submersible observations of sewage disposal at the Maryland Ocean Dumpsite there is evidence that a surficial blanket does form near the bottom and breaks up only when storm-induced mechanical energy causes forced mixing. The result is that ridges of ocean bottom are clear of this floc and that swails tend to accumulate this material. In all probability this same effect will be realized from the dumping of spent stone granules.

Another experiment was conducted to measure the heat released as a result of mixing CAFB stone in seawater. Once again approximately 50 gms of granular spent stone was placed into a 1 liter settling tube. The ambient seawater temperature was 14.2°C. Thermisters placed in the sediment, at mid-water and at the water surface were monitored and temperatures plotted from the time the stone was dumped into the settling tube. Figure 7 shows these results which indicate that the maximum increase in temperature was 10.4°C over ambient and occurred 19 minutes after the start. Projecting the curves in Figure 7 equilibrium temperatures would be reached within 1 hour after dumping.

A final experiment was conducted whereby the phases of the spent stone in seawater were isolated and chemical analysis performed on the solid and liquid fractions. In this test 50 g/l were mixed, pH recorded over a 24-hour period and the samples allowed to settle into distinct layers. Heavy metals analysis was performed on liquid and solid fractions of CAFB stone/seawater mixtures. Results of the pH data are given in Table 5 and the metals analysis are shown with a comparison to other ocean dumpsite data in Table 6. From these results it appears that only Vanadium shows any significant increase over ambient levels expected in seawater.

From the initial assessments made by the Ocean Reasearch Laboratory we believe it may be possible to secure an interim permit for ocean disposal of spent stone. Our initial judgement is based on certain precedents which have been set as well as the specific requirements in the Final Regulations. Some questions have arisen with regard to the amended regulations. Spent stone waste disposal permits may be secured under the regional permit system in the North and Mid-Atlantic, as well as Western Gulf states. This includes areas covered by Region I in Boston, Region II in New York, Region III in Philadelphia and Region VI in Dallas as they are the only EPA regional offices with jurisdiction over active industrial dumpsites. Region IV which includes the Southeastern Atlantic and Eastern Gulf states does not have any designated industrial dumpsites and would reguire and inter-regional permit. This would be possible, but more difficult to obtain through the administrator's office in Washington.

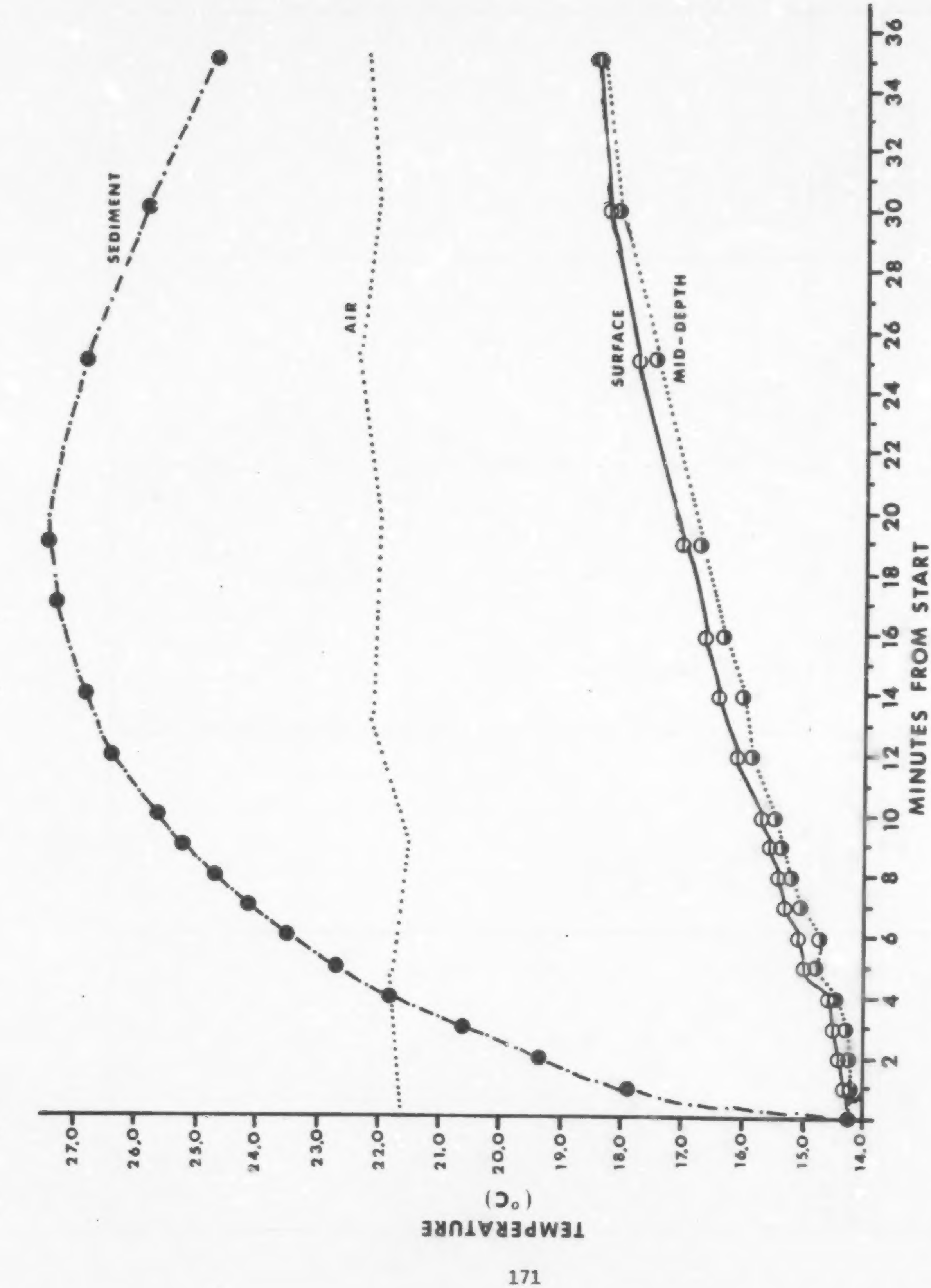

Figure 7. Temperature Changes with CAFB/Seawater Mixture

Table 4. Suspended Particulates From CAFB/Seawater Mixtures

TIME			SURFACTANT FRACTION		FLOCCULANT FRACTION	
MINUTES MIXED		HOURS SETTLED	% OF TOTAL LIQUID	CONCENTRATION (mg/ℓ)	% OF TOTAL LIQUID	CONCENTRATION (mg/ℓ)
1	—	1	8.5	340	91.5	279×10^1
2	—	1	25.1	179	74.9	289×10^1
1	—	3	77.2	37.8	22.8	393×10^1
2	—	3	83.1	94.6	16.9	112×10^2
2	—	18	82.8	11.9	17.2	159×10^2

Table 5. Changes in pH with CAFB Mixed in Seawater

TIME (HOURS)	pH
START	9.75
0.25	11.85
0.50	11.95
0.75	12.00
1.00	12.00
6.00	12.25
12.00	12.40
18.00	12.50
24.00	12.80

Table 6 Heavy Metals Evaluation of CAFB Stone Compared to Other Ocean Dumpsites

ELEMENT	DUMPSITE LOCATION	* COMPARABLE DUMPSITE DATA:					** CAFB SPENT STONE:		
		N.Y. Bight (EPA)	Mid-Atlantic Bight Sewage Disposal Site (EPA)	Mid-Atlantic Bight-Shellfish Data	N.Y. Bight Army Corps of Engineers	Mid-Atlantic Bight Acid Disposal Site (EPA)	Water Mixture (ppm in solution)	Separation Experiment Liquid Fraction	Separation Experiment Solid Fraction
Chromium	Dump	43	2		Range 1.8-460.0 Mean 60.7	200	< 0.02	<0.3	<0.2
	Control	<34							
Copper	Dump	<53	<1	7.52	Range 1.5-330.0 Mean 6.32	8	0.2	0.8	0.6
	Control	<32		6.33					
Nickel	Dump	<15		4.13	Range 3.0-45.0 Mean 13.9	16	<0.02	<0.3	<0.2
	Control	<12		2.11					
Lead	Dump	<88		3.37	Range 7.0-700.0 Mean 102.5	52	<0.02	<0.2	<0.2
	Control	<75		3.51					
Zinc	Dump		6		Range 9.0-900.0 Mean 141.9	110	<2.5	<2.5	<2.5
	Control		8						
Silver	Dump			3.73		1.2	1.3	0.08	<0.06
	Control			1.18					
Iron						50,000	0.2	0.3	0.2
Manganese						1,700	<.07	<.07	<.07
Antimony						10	<2.0	<2.0	<2.0
Titanium						3,000	<1.0	<1.0	<1.0
Vanadium						220	7.0	8.0	13.0
$CaCO_3$						225,000 (a measure of acidity)			

* ppm concentrations in sediments.
** ppm concentrations in fractions indicated.

Specific requirements in the EPA Final Regulations which provide the mechanism for ocean dumping are contained in Part 227, Sections 227.3, 227.4, and 227.5. Certain classifications within these sections must be made concerning the applicability of spent stone wastes to ocean disposal. According to Section 227.31 (b), such elements as Nickel and Vanadium must not be available in the waste atconcentrations greater than 0.01 of the concentration established to be toxic to biota of the receiving waters. While the evaluation criteria does allow for a mixing zone, special care must be taken with elements in the waste which are normally found in seawater at trace concentrations (less than 1 part per million). Section 227.34 of the Final Regulations also identifies the considerations which must be given to the alkalinity of the waste disposal. Because of the high pH caused by mixing of the spent stone and water there may be a potential for synergistic effects or the formation of toxic compounds to be found during the immediate release process. This matter must be clarified further before proceeding with a permit consideration.

The most important section of the Final Regulations regarding feasibility of spent stone disposal is contained in Section 227.4 which establishes the implementation plan requirements for interim permits. This includes the necessary planning and implementation phase for securing ocean dumping permits. The most critical issue in this section states that for industrial wastes the dumper must "(a) demonstrate the need for proposed dumping...compared to alternative locations and methods, (b) demonstrate the need for the proposed dumping outweights the potential harm...and (c) provide as satisfactory implementation plan...of the best practical technology currently available for removal of such materials." This also includes the best economically available technology for waste removal.

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APPENDIX VB

OCEAN DUMPING

From Environmental Systems Department
WIN 236-7146
Date February 1, 1977
Subject Ocean Dumping

R & D CENTER - BLDG. 501 3E19

To W. G. Vaux

The following memorandum describes the results of my assessment of the Environmental Protection Agency's (EPA) attitude toward ocean dumping and the kinds of studies required by EPA to obtain a permit for ocean dumping. The purpose of the assessment as defined in Work Order 34-JP-CPFF-935644-L-A (WESD Contract #743) was to determine: (1) EPA's attitude toward ocean disposal of sulfated and sulfided limestone in all contiguous U.S. EPA Regions with emphasis on Regions VI and III, (2) estimate the probability of EPA issuing an ocean disposal permit in calendar year 1977 and between 1978 and 1983 inclusive and (3) determine what preliminary bench-scale dispersion and biotoxicity test will satisfy current EPA requirements.

These three objectives were met by contacting EPA Regional Offices and research laboratories and reviewing rules and regulations as reported in the Federal Register. From these contacts and reviews, it is concluded that obtaining a permit from EPA to dump waste on a commercial scale would be extremely difficult in either 1977 or between 1978 and 1983 because of the general policy of EPA to phase out all ocean disposal of industrial waste by 1981. The feasibility of ocean dumping is further limited by the kinds of constituents associated with the waste and the regulatory requirements to perform a detailed environmental assessment of the waste and monitor the dump site. Reasons leading to these conclusions are presented in detail in the following paragraphs.

EPA Regions III and VI and the Environmental Research Laboratory in Narragansett, Rhode Island were contacted regarding EPA policy. Region III indicated that EPA in all regions is currently attempting to phase out ocean dumping of industrial waste by 1981.(1) Region III summarized the situation in each region as follows:

> Region I (Boston) has at present only two existing ocean disposal permits. Region II (New York) where most of the ocean dumping is currently taking place, has currently eliminated approximately 50 industrial dumping permits and most others are on a compliance schedule to phase out dumping by 1981. Region III

(Philadelphia) has one ocean dumping permit which will be eliminated by 1980. No ocean dumping of industrial waste, is being conducted in either Region IV (Atlanta), Regions IX (San Francisco) or Region X Seattle).

Of the seven dumping permits issued in Region VI (Dallas) only two are operational.(2) Region VI is currently being sued by a local fishing group for having allowed ocean dumping.

Conversations with personnel at the EPA Environmental Research Laboratory who are involved in assessing effects of ocean dumping, concurred that EPA is currently attempting to phase out ocean dumping.(3,4) When the type of waste being considered was described to one of the staff responsible for research activities, he felt that the vanadium content would preclude it from meeting ocean dumping criteria and that the waste might also contain higher than allowable mercury levels, particularly if the facility is to be fitted with scrubbers.(4)

EPA has promulgated regulations and criteria governing ocean dumping pursuant to Title I of the Marine Protection, Research and Sanctuaries Act of 1972, Public Law 92-532. Regulations and criteria were published in the Monday, October 15, 1973 Federal Register. Proposed revisions of these regulations and criteria were published in the Monday, June 28, 1976 Federal Register, and final revisions of regulations and criteria were published in the Tuesday, January 11, 1977 Federal Register. The January 11, 1977 regulations and criteria are the effective regulations and were reviewed to determine kinds of studies to be conducted in order to obtain a permit.

The regulations and criteria issued January 11, 1977 identify six basic types of permits. These are general permits, special permits, emergency permits, interim permits, research permits and permits for incineration at sea. General permits may be issued for the dumping of materials which have a "minimal adverse environmental impact and are generally disposed of in small quantities, or for specific classes of materials that must be disposed of in emergency situations." Special permits may be issued for the dumping of materials which satisfy criteria (refers to criteria described in January 11, 1977 Federal Register which are discussed below) and shall expire no later than 3 years from the date of issue. Emergency permits may be issued to dump such materials where there is demonstrated to exist: "an emergency requiring the dumping of such materials, which poses an unacceptable risk relating to human health and admits of no other feasible solution." Interim permits may be issued prior to April 23, 1978 to dump materials which are not in compliance with the environmental impact criteria or which would cause substantial adverse effects as determined by the criteria or for which an ocean disposal site has not been designated on other than an interim basis. A permittee may continue to dump past the April 23, 1978 deadline if the permittee has an implementation schedule to phase out ocean dumping by December 31, 1981 or if he can meet the requirements of a special permit. In addition, no interim permit will be granted for the dumping of waste from a facility which has not previously dumped wastes in the ocean, from a new facility or for the dumping of an increased amount of waste from the expansion or modification of an existing facility. Research permits may be issued for the dumping of materials into the ocean as part of a research project when it is determined that the "scientific merit of the proposed project outweighs the potential environmental or other damage that may result from the dumping." Permits for incineration at sea may be issued in special cases but are not applicable to disposal of spent stone from fluidized bed combustion.

By considering the types of permits issued, only an interim permit and special permit are applicable for the disposal of the spent stone on a commercial scale. However, no interim permits will be issued to new facilities and existing interim permits will be eliminated by 1981 such that all ocean dumping of industrial waste must be in compliance with the rules and regulations of a special permit. Therefore, it is concluded that ocean dumping of spent stone from fluidized bed combustion process is possible only if provision of a special permit can be met. Criteria for evaluation of permit applications for ocean dumping and criteria for management od disposal sites for ocean dumping are presented in Parts 227 and 228 or the "Final Revision of Regulations and Criteria" published in the January 11, 1977 Federal Register.

Criteria for the evaluation of permit applications for ocean dumping require an assessment of the environmental impact, the need for ocean dumping, impact of the proposed dumping on esthetic, recreational and economic values and impact of the proposed dumping on other uses of the ocean. Even if an applicant demonstrates that the material to be dumped staisfies environmental impact criteria, a permit may be denied if the other criteria are not met.

Ocean dumping criteria prevent disposal of certain compounds including mercury and mercury compounds and cadmium and cadmium compounds. Spent stone could contain significant amount of these substances, depending on the source of limestone and coal.

To assess the environmental impacts, it is necessary to conduct extensive bioassays. These bioassays must be conducted on the liquid, suspended particulate and solid phases to demonstrate at the 95 percent confidence level, that when materials are dumped, no significant, undesirable effects will occur. In addition to determination of lethal effects, the possibility of sublethal effects due to bioaccumulation must be considered. Bioassay tests shall be conducted on at least one species each of phytoplankton or zooplankton, crustacean or mollusk and fish. Chronic toxicity and bioaccumulation of the solid phase shall be conducted on benthic organisms, including at least one species each representing a filter-feeding, deposit feeding and burrowing species. Therefore, these bioassay and bioaccumulation studies must be conducted on a total of at least six different test organisms.

The liquid phase of a material is defined as the supernatant remaining "after 1 hour undisturbed settling, after centrifugation and filtration through a 0.45 micron filter." The suspended particulate phase is the "supernatant as obtained above prior to centrifugation and filtration" and the solid phase includes all material settling to the bottom in 1 hour.

It is also necessary to determine if the liquid phase after allowance for initial mixing (dispersion which occurs within 4 hours after dumping) meets water quality criteria contained in "Quality Criteria for Water."(5) A permit may also be denied if "mercury and its compounds are present in any solid phase in concentrations greater than 0.75 mg/kg or more than 50 percent greater than the average total mercury of natural sediments of similar lighographic characteristics as those at the disposal site" or cadmium and its compounds are present "in amy solid phase of material in concentrations less than 0.6 mg/kg or less than 50 percent greater than the average total cadmium content of natural sediments of similar lithographic characteristics as those at the disposal site."

In disposing of alkaline waste such as the spent stone, dumping conditions must be such that the total alkalinity after allowance for initial mixing may be changed based on stoichiometric calculations by no more than 10 percent during all dumping operations. To meet this criterion, it would involve a thorough analysis of proposed dumping procedures and dispersion of the waste. Models for predicting disposal of a substance containing both solid and soluble phases such as spent stone are not available at this time.(6,7) If no feasible means is available for estimating dispersion, the liquid and solid phases may be assumed to be evenly distributed after 4 hours over a column of water bounded on the surface by an area swept out by the locus of points constantly 100 meters from the perimeter of the dumping point and extending to the ocean floor, thermocline or halocline, if one exists, or to a depth of 20 meters whichever is shallower.

Need for ocean dumping must also be demonstrated. Particular attention should be given to the relative environmental risks, impact and cost for ocean dumping as opposed to other feasible alternatives, including but not limited to: (1) land fill, (2) well injection, (3) incineration, (4) spread of material over open ground, (5) recycling of material for reuse, (6) additional biological, chemical or physical treatment or intermediate or final waste streams and (7) storage.

If a potential ocean dumper meets all criteria and regulations and obtains a permit, the EPA Regional Administrator has the authority to require the permittee to conduct a monitoring program at the dump site. If it is determined that the waste to be dumped is not compatible with waste being dumped at an existing site, the EPA may require the selection of a new dump site. If a new site is designated, the permittee must conduct a base line monitoring program at the site.(1)

In summary, EPA is currently attempting to phase out ocean dumping of industrial waste by 1981. However, if a potential ocean dumper can meet the stringent criteria of a special permit, a possibility exists for a permit to be granted. Criteria to be met include not only physical/chemical characterization and bioassay of the material to be dumped but also full evaluation of alternatives followed by mointoring of the dump site if a permit is issued. The possibility that this particular waste contains constituents such as vanadium, mercury and arsenic from combustion of coal and is highly alkaline suggests that it will not meet criteria.

The policy of EPA to phase out ocean dumping of industrial waste by 1981, the stringent criteria which must be meet to obtain a special permit and the cost associated with demonstrating compliance with the criteria preclude, in my opinion, consideration of ocean dumping as a means of disposal of sulfated and sulfided limestone waste from the fluidized bed combustion process on a commercial scale.

Henry A. Donaldson
Aquatic Biological Sciences

HAD:knw

cc: M. Kirshner
G. A. Valiulis
C-743

APPENDIX B

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APPENDIX C

PREDICTED PRODUCTION PROPORTIONS OF SPENT SORBENT AND FLY ASH FROM FLUIDIZED BED COMBUSTION

Let

X_S = weight fraction of total sulfur in the fuel
X_A = weight fraction of ash in the fuel
X_I = weight fraction of inerts in the fresh sorbent
R = Ca/S molar treat ratio

Then, on the basis of 100 kg of fuel fed, the fly ash production is

$$W_A = 100\ X_A$$

The sorbent feed rate is

$$W_L = \left(\frac{100\ X_S}{M_S}\right) R\ M_L \text{ in the case of limestone}$$

and

$$W_D = \left(\frac{100\ X_S}{M_D}\right) R\ M_D \text{ for dolomite}$$

where M_S, M_L and M_D are the molecular weights of sulfur, calcium carbonate and pure dolomite, respectively.

Let

S_R = fraction of feed sulfur retained by the sorbent

The products may contain CaO, $CaSO_4$, $CaCO_3$, fuel ash and limestone inerts in the case of limestone and CaO•MgO, $CaSO_4$•MgO, $CaCO_3$•MgO, fuel ash and dolomite inerts in the case of dolomite. The two cases can be treated as one by writing the sorbent as $CaCo_3 \cdot aMgCO_3$ where a = Mg/Ca molar ratio in the fresh sorbent and is 1 for dolomite and 0 for limestone. The dolomite feed rate is then:

$$W_D = (\frac{100\ X_S}{M_S})\ R\ [M_L + a\ M_M]$$

where M_M is the molecular weight of magnesium carbonate.

The production rate of spent sorbent is then as follows. (these calculations assume that magnesium is fully calcined to oxide, and the calcium is distributed among oxide, sulfate and carbonate):

Let

a_L = fraction of feed $CaCO_3$ surviving calcination

Then

$$(CaCO_3 + a\ MgO) = a_L\ [(\frac{100\ X_S}{M_S})\ R]\ [M_L + a\ M_N]$$

$$(CaSO_4 + a\ MgO) = S_R\ [(\frac{100\ X_S}{M_S})]\ [M_A + a\ M_N]$$

$$(CaO + a\ MgO) = [(1 - a_L)\ R - S_R]\ [\frac{100\ X_S}{M_S}]\ [M_Q + a\ M_N]$$

where M_N, M_A, and M_Q are the molecular weights of magnesia (MgO), anhydrite ($CaSO_4$) and quick lime (CaO), respectively. The insert content in the output is

$$W_I = (\frac{X_I}{1 - X_I})\ [(\frac{100\ X_S}{M_S})\ R]\ [M_L + a\ M_M]$$

The spent sorbent production rate is then the sum of the above four expressions which can be reduced to:

$$W_{SS} = [\frac{100\ X_S}{M_S}]\ \{R\ [(\frac{M_O + a\ M_N}{1 - X_I}) + M_C\ (a_L + (1 + a)\ \frac{X_I}{1 - X_I})] + S_R\ M_T\}$$

where M_C and M_T are the molecular weights of carbon dioxide and sulfur trioxide, respectively.

The sorbent/fly ash ratio, assuming a sharp separation, is

$$\frac{W_{SS}}{W_A} = (\frac{X_S}{X_A})(\frac{1}{M_S})\ \{R\ [(\frac{M_O + a\ M_N}{1 - X_I}) + M_C\ (a_L + (1 + a)\ \frac{X_I}{1 - X_I})] + S_R\ M_T\}$$

Inserting molecular weights and typical values as $a = 1.0$, $S_R = 0.90$, $a_L = 0.0$, $X_A = 0.10$, $X_I = 0.05$, this yields:
for limestone

$$\frac{W_{SS}}{W_A} = X_S\ [19.1353\ R + 22.4747]$$

for dolomite

$$\frac{W_{SS}}{W_A} = X_S\ [33.0929\ R + 22.4747]$$

These equations are plotted in Figure C-1.

Curve 686999-A

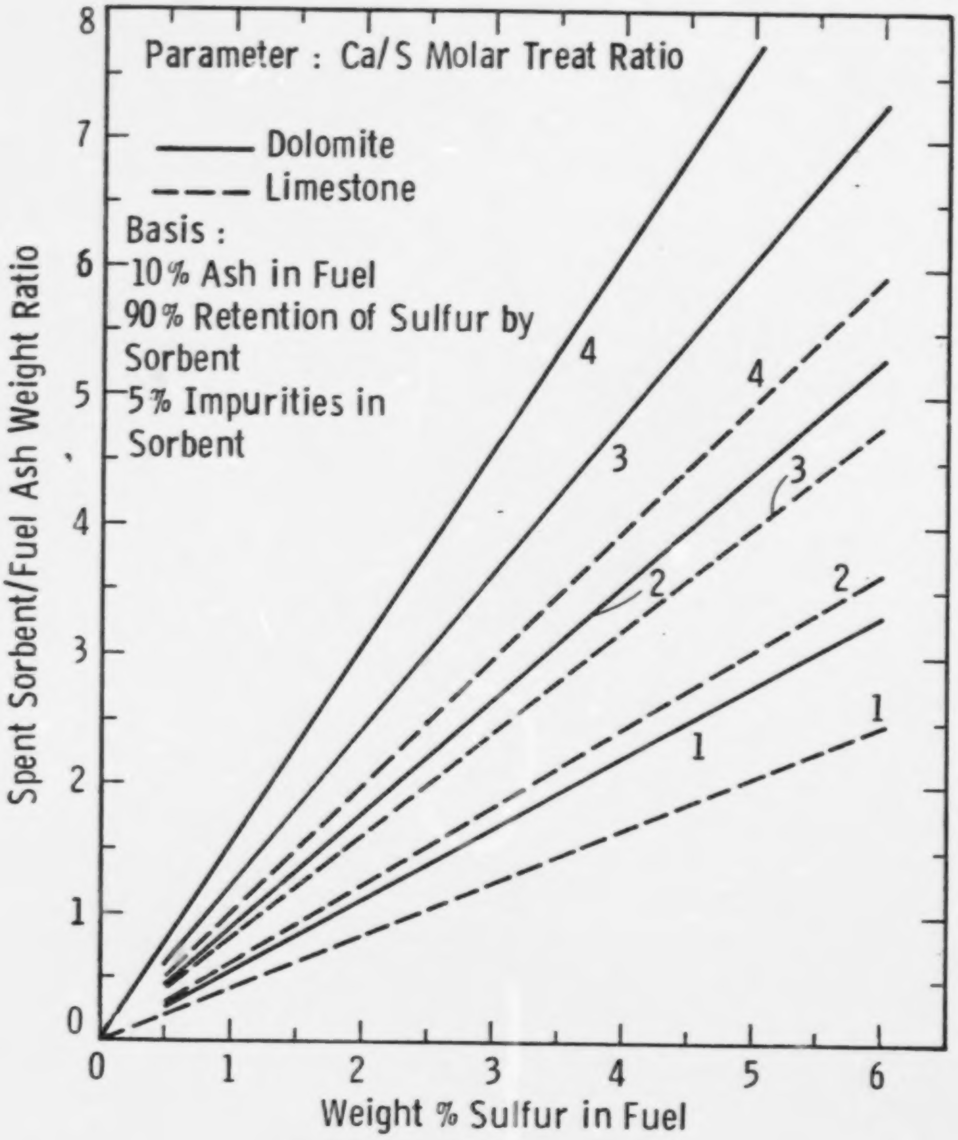

Figure C-1. Spent Sorbent/Fuel Ash Ratio in Fluidized-Bed Combustion